Intramolecular γ C–H Insertion *vs.* Olefin Cycloaddition in 4-Methylene-2-adamantylidene and 8-Methylene-2-noradamantylidene

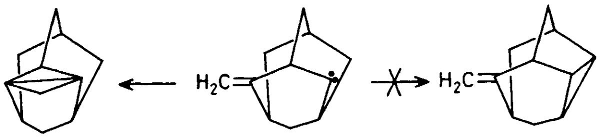
Zdenko Majerski,* Zdenko Hameršak, and Katica Mlinarić-Majerski
Rudjer Bošković Institute, 41001 Zagreb, Croatia, Yugoslavia

8-Methylene-2-noradamantylidene inserts readily into the γ C–H bond giving 6-methylene-2,4-didehydronoradamantane rather than the olefin-cycloaddition product, while its higher homologue 4-methylene-2-adamantylidene reacts exclusively by intramolecular cycloaddition to the olefinic bond yielding 2,4-methano-2,4-didehydroadamantane, a [3.1.1.]propellane.

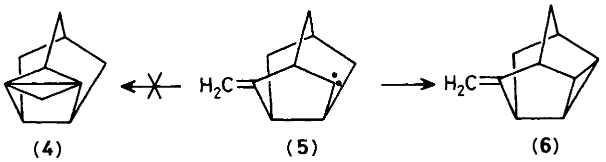
An intermolecular carbene cycloaddition to an ethylene leading to a cyclopropane is a facile process requiring no energy of activation.[1] Intermolecular insertions of a carbene into C–H bonds are highly unselective processes indicating that the respective activation energies are very small.[1b] However, *intramolecular* carbene cycloadditions to olefinic bonds as well as insertions into C–H bonds may involve highly strained transition states and appreciable activation energies.

2-Adamantylidene inserts readily into the γ C–H bond giving rise to 2,4-didehydroadamantane as the only product.[2] However, 4-methylene-2-adamantylidene (**2**) reacts exclusively by intramolecular cycloaddition to the olefinic bond producing 2,4-methano-2,4-didehydroadamantane, a [3.1.1] propellane, (**1**),† in 70% yield.[3] No C–H insertion product [methylene-2,4-didehydroadamantane, *e.g.* (**3**)] was detected by ^1H and ^{13}C n.m.r. spectroscopy. Both carbenes, 2-adamantylidene and (**2**), were generated by pyrolyses of the respective dry tosylhydrazone alkali salts *in vacuo*. The products sublimed into traps cooled by liquid nitrogen. The spatial arrangements of the γ C–H bonds in relation to the carbenic centre in 2-adamantylidene are virtually the same as in 4-methylene-2-adamantylidene (**2**). Consequently, the activation energy for the cycloaddition of carbene (**2**) leading to (**1**) must be smaller than that for the competitive γ C–H insertions, although the cycloaddition product (**1**) is 40 kcal mol^{-1} (1 kcal = 4.184 kJ) more strained than the insertion product of 2-adamantylidene, 2,4-didehydroadamantane.‡

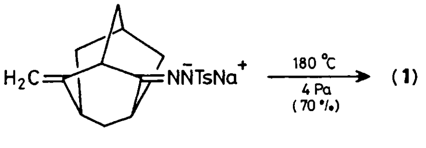
8-Methylene-2-noradamantylidene (**5**), contrary to its higher homologue 4-methylene-2-adamantylidene (**2**), gave exclusively the γ C–H insertion product, 6-methylene-2,4-

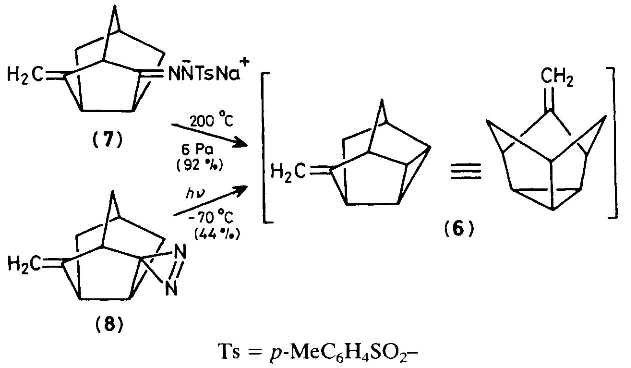


(**1**) (**2**) (**3**)



(**4**) (**5**) (**6**)





(**7**) (**8**) (**6**)

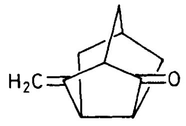
Ts = p-$MeC_6H_4SO_2$–

---

† The crude product (**1**) was ⩾95% pure (by ^{13}C n.m.r.). ^{13}C n.m.r. (C_6D_6) δ 64.4 (d, *J* 166 Hz, 1 C), 50.1 (t, *J* 129 Hz, 1 C), 40.9, (dd, *J* 151, 169 Hz, 1 C), 44.0 (d, *J* 138 Hz, 2 C), 34.2 (t, *J* 128 Hz, 2 C), 30.8 (t, *J* 129 Hz, 1 C), 26.6 (d, *J* 133 Hz, 1 C), 24.2 (s, 2 C); ^1H n.m.r. (C_6D_6) δ 2.36—1.06 (multiplet with two distinctive doublets at δ 2.12 and 1.08, *J* 4 Hz); i.r. (KBr) 3040 (w), 2905 (s), 2850 (m), 1462 (m), 1450 (m), 1330 (m), 1190 (m), 1070 (m), 1020 (w) cm^{-1}; *m/z* (rel. intensity) 146 (M^+, 65), 131 (85), 117 (60), 105 (91), 104 (83), 92 (46), 91 (100), 79 (45), 77 (40).

‡ The strain energies of (**1**) and 2,4-didehydroadamantane were calculated to be 83.9 and 43.5 kcal mol^{-1}, respectively, by using the MM2 force field (U. Burkert, personal communication).

didehydronoradamantane (**6**),§ rather than the cycloaddition product (**4**).¶ Carbene (**5**) was generated either by pyrolysis of the dry tosylhydrazone sodium salt of 8-methylene-2-noradamantanone (**7**) *in vacuo* or by photolysis of the corresponding diazirine (**8**) at −70 °C in $[^2H_8]$toluene.|| The former method yielded 92% and the later 44% of (**6**).



(**9**)

The electrophilic carbenic centres in (**2**) and (**5**) appear to interact through space with both the olefinic π-electrons and the C–H σ-electrons.[5] However, the cycloaddition transition state of carbene (**2**) is energetically more favoured than that of the insertion, while the cycloaddition transition state of carbene (**5**) is highly strained and energetically less favoured than the insertion transition state. Hence, carbene (**2**) yields exclusively the cycloaddition product (**1**) and carbene (**5**) the insertion product (**6**).

We thank the Research Council of the Republic of Croatia for financial support.

Received, 19th July 1985; Com. 1052

---

§ The crude product (**6**) was $\geqslant$98% pure (by g.c.). ^{13}C n.m.r. (C_6D_6) δ 165.1 (s, 1 C), 96.5 (t, 1 C), 49.6 (t, 2 C), 45.7 (d, 2 C), 40.3 (d, 1 C), 36.8 (d, 1 C), 35.1 (d, 2 C); ^{1}H n.m.r. ($CDCl_3$) δ 4.31 (s, 2 H), 2.9—1.2 (m, 10 H); i.r. (film) 3045 (m), 2950 (s), 2860 (m), 1668 (m), 1446 (w), 1315 (w), 872 (m), 772 (m), 670 (m) cm^{-1}; *m/z* (rel. intensity) 132 (M^+, 47), 117 (82), 91 (100), 78 (59); satisfactory elemental analyses were obtained.

¶ The possibility of formation of the cycloaddition product, 2,8-methano-2,8-didehydronoradamantane (**4**) cannot be absolutely excluded on the basis of these results. Such a thermodynamically unstable molecule could possibly isomerize back to 8-methylene-2-noradamantylidene (**5**) by a retro-carbene ring opening even at −70 °C. This eventuality was eliminated by deuterium labelling. 8-Methylene-2-noradamantylidene-4-*endo*-$[^2H_1]$ gave 6-methylene-2,4-didehydronoradamantane (**6**) deuteriated exclusively at position 2 rather than the isotopomer having deuterium scrambled. The full details of this work will be published elsewhere.

|| 8-Methylene-2-noradamantanone (**9**), $\geqslant$98% pure by g.c., was prepared in 32% overall yield by methyl Grignard addition to 8-*exo*-hydroxy-2-noradamantanone,[4] followed by dehydration of the resulting tertiary alcohol group with iodine and Jones oxidation of the secondary hydroxy function. The tosylhydrazone sodium salt (**7**) was prepared from ketone (**9**) following standard procedures. Diazirine (**8**) was obtained in 44% overall yield by a treatment of (**9**) with a freshly prepared solution of hydroxylamine-*O*-sulphonic acid in liquid ammonia, followed by oxidation of the resulting diaziridine with silver oxide and purification of the crude product by column chromatography. Ketone (**9**) and diazirine (**8**) have been fully characterized by spectral means and gave satisfactory elemental analyses.

References

1 (a) R. Hoffmann, *J. Am. Chem. Soc.*, 1968, **90**, 1475; (b) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, 1972, **94**, 9095.

2 A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Commun.*, 1966, 657; S. D. Isaev, A. G. Yurchenko, F. N. Stepanov, G. G. Koljada, S. S. Novikov, and N. F. Karpenko, *Zh. Org. Khim.*, 1973, **9**, 724.

3 K. Mlinarić-Majerski and Z. Majerski, *J. Am. Chem. Soc.*, 1980, **102**, 1418; K. Mlinarić-Majerski and Z. Majerski, *ibid.*, 1983, **105**, 7389.

4 Z. Majerski and Z. Hameršak, *J. Org. Chem.*, 1984, **49**, 1182.

5 R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, 1968, **90**, 5457; R. A. Moss and U.-H. Dolling, *Tetrahedron Lett.*, 1972, 5117; R. A. Moss, U.-H. Dolling, and J. R. Whittle, *ibid.*, 1971, 931; R. A. Moss and C.-T. Ho, *ibid.*, 1976, 1651; M. H. Fisch and H. D. Pierce, Jr., *Chem. Commun.*, 1970, 503.