Dehydroprotoadamantanes. Intramolecular Insertion Reactions of 4- and 5-Protoadamantylidene

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Summary Pyrolyses of tosylhydrazone sodium salts of 4- and 5-protoadamantanone produced, in addition to protoadamantene, 2,4-dehydroadamantane and 5,7-dehydroprotoadamantane, respectively; the carbene appears to approach with its empty *p*-orbital towards the nearest C–H bond of suitable geometry to form the product.

Although intramolecular carbene insertions have been used for the preparation of many strained polycyclic hydrocarbons,[1] little is understood of these reactions.[2]

We now report the intramolecular insertion reactions of 4- and 5-protoadamantylidene, (**1a**) and (**2a**), produced by pyrolyses of the corresponding tosylhydrazone sodium salts (**1**) and (**2**).† The carbene (**1a**) yielded a mixture of protoadamantene (**3**) and 2,4-dehydroadamantane (**4**) in the ratio of 1:4·5, while (**2a**) gave a mixture of (**3**) and an unknown hydrocarbon in the ratio of 1:1·6.‡ Protoadamantene and 2,4-dehydroadamantane were identified by ^{1}H n.m.r. and i.r. spectroscopy, mass spectrometry, and g.l.c. in comparison with authentic samples.[1a,3d] The major product of (**2**) was expected to be one of three dehydroprotoadamantanes: (**5**), (**6**), or (**7**). It had a longer g.l.c. retention time than (**3**), and had the following spectral properties: *m/e* 134 (68%), 119 (27%), 105 (22%), 92 (100%), 79 (88%), i.r. (KBr) 3020m, 2930s, 2858m, 1450m, 1440m, 1022m, 755m, and 702m cm^{-1}, ^{1}H n.m.r. (CDCl$_3$) δ 0·5—2·7 p.p.m. (broad, complex multiplet). Hydrogenolysis of this compound in glacial acetic acid (50°, 4 atm.) over a Pt-catalyst yielded a single product which gave a parent-ion signal at *m/e* 136.§ This indicates a dehydroprotoadamantane structure containing a cyclopropane ring, (**5**) or (**6**). The proton-decoupled ^{13}C n.m.r. spectrum shows ten signals at 42·8, 41·4, 40·6, 37·9, 35·0, 32·7, 28·9, 26·4,

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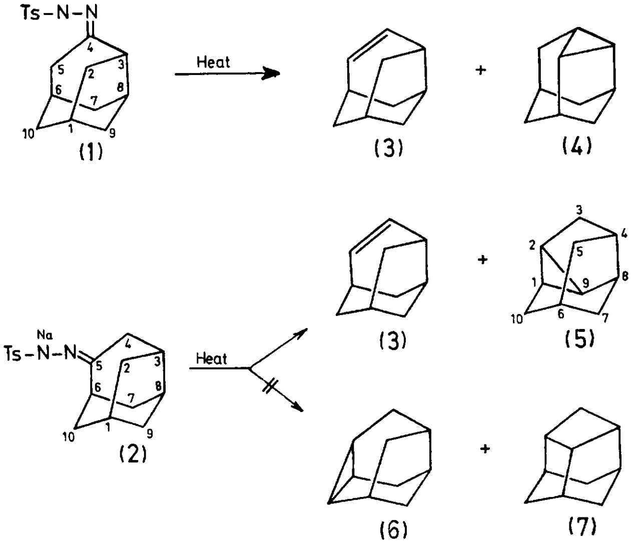
† The tosylhydrazone salts were obtained by standard procedures[1b] from the corresponding ketones.[3] The pyrolyses were carried out at 180—200° (0·1 mm) for 1—2 h in a sublimator. Both salts gave mixtures of sublimable products in overall yields of 40—45%. The products were analysed and separated by g.l.c. (10% FFAP, 70°, and 10% Apiezon L, 120°, respectively).

‡ A small amount (*ca.* 5%) of an unidentified compound was also produced.

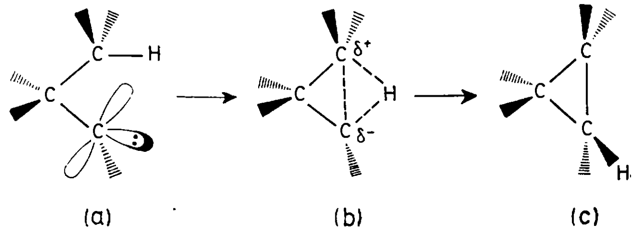
§ The hydrogenated product had the same g.l.c. retention time (10% FFAP, 70°) as protoadamantane but different from that of 9-homonoradamantane.[4] An authentic sample of the third possible product, tricyclo[4.2.1.1^{4,9}]decane, was not available.

23·6, and 12·3 p.p.m. which correspond to 5,7-dehydroprotoadamantane (**5**), tetracyclo[4.3.1.$0^{2,9}0^{4,8}$]decane).



The initial approach of a carbene to a C–H bond appears to be different in intermolecular and intramolecular carbene insertions. The most favoured approach of CH_2 in the intermolecular insertions was shown to be with its empty *p* orbital along the axis of the C–H bond.[5] In the intramolecular insertions such an approach is usually impossible and a carbene must take a geometrically less favoured way. (The later insertions are still highly preferred due to the proximity of the carbene to the C–H bond).

The preferential formation of the dehydroprotoadamantanes (**4**) and (**5**) could be explained by the approach of the carbene with its empty *p* orbital towards the nearest γ C–H bond of suitable geometry [Figure (a)], to form the transition state (b)¶ and then the cyclopropane product (c). The direction of the intramolecular carbene insertions thus appears to be governed by the proximity and the geometry of the carbene *p* orbital to the C–H bonds. The olefin is probably produced through a similar transition state formed by the approach of the carbene empty *p* orbital to the slightly divergent β C–H bond. The products of previously reported intramolecular carbene insertions[1] are in accord with this hypothesis. In addition to proximity and geometry of the carbene in relation to the C–H bond, other factors, like product stability,[7] should also be taken into consideration.



FIGURE

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¶ A similar transition state has been proposed recently for the intermolecular insertions of CCl_2 into C–H bond.[6]

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