# Gas-phase Reactions on Platinum. Mechanism of the 1,2-Bond Shift Rearrangement of Alkanes

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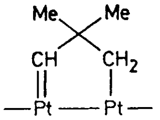
*Summary* The mode of expansion of the four membered ring in the {2+2} dimers of adamantane in the gas phase on platinum indicates that the removal of one bridgehead hydrogen atom on the metal surface is a sufficient requirement for rearrangement.

Skeletal rearrangement of simple alkanes, such as neopentane → isopentane, is catalysed at elevated temperatures by noble metals, especially platinum.[1,2] This behaviour has been attributed to the formation and further reaction of an ααλ-triadsorbed intermediate (**1**) bonded to two contiguous metal atoms.[1] An essential feature of this proposal is the requirement that three hydrogen atoms be lost from the alkane in forming the surface intermediate.



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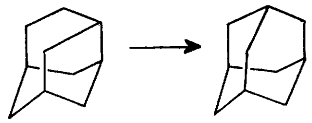
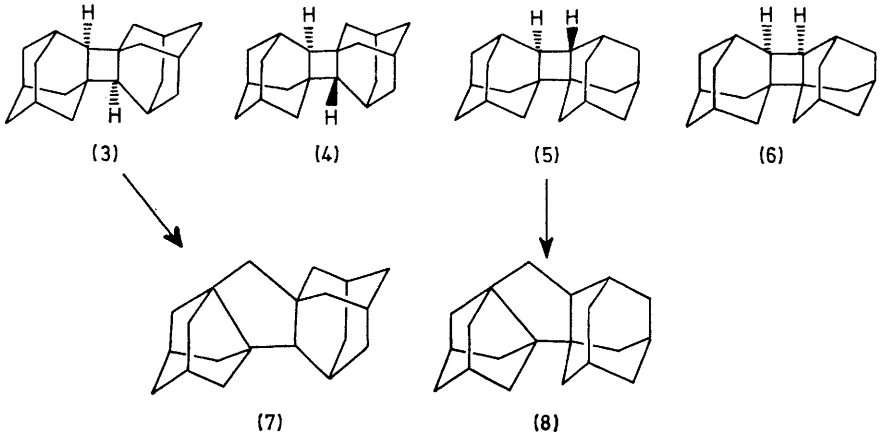


(2)

However, it has been argued[3,4] on simple geometric grounds alone that the ααλ mechanism may not be universally applicable since cases are known in which formation of the required intermediate is very unfavourable structurally. The protoadamantane → adamantane rearrangement (**2**) is such a case, yet the change occurs readily on platinum with 100% selectivity and an activation energy of 10·1 kcal mol$^{-1}$ (160—300 °C).[4] An alternative suggestion is that loss of a single hydrogen atom from the alkane is sufficient to initiate rearrangement, *i.e.* essentially covalently bonded alkyl groups rearrange on a platinum surface in a manner commonly observed with carbonium ions. We have obtained confirmatory evidence in support of this suggestion.

Two of the four possible {2+2} dimers, (**3**)—(**6**), of the highly strained transitory olefin adamantene have been isolated[5,6] and assigned the *syn-trans*-structure (**3**) and the *anti-cis*-structure (**5**) on $^{13}$C n.m.r. spectroscopic evidence.[6] Dimers (**3**) and (**5**) are unusual in that unlike most cyclobutanes they do not suffer hydrogenolytic opening of the C$_4$ ring in the gas phase on platinum at elevated temperatures. When a 2:1 mixture of (**3**) and (**5**) was passed over platinum in hydrogen at 210 °C two new hydrocarbons (ratio 2:1), isomeric with (**3**) and (**5**), were produced in quantitative yield; both products were stable towards hydrogenolysis on platinum at 350 °C, suggesting that the cyclobutane ring was no longer present.

Empirical force field calculations[7] were used to probe the structures and enthalpies of the dimers and the energetics of possible rearrangements of isomers (**3**) and (**5**). The data[7] (Table) indicate all four dimers to be highly strained, the least stable being the unknown isomers (**4**) and (**6**). Strain analysis reveals that the adamantane skeleton in (**3**) and (**5**) is distorted slightly, but this distortion is minimal compared with that of the cyclobutane ring. Bending strain is much larger than nonbonded strain and the latter largely involves the hydrogen atoms attached directly to the cyclobutane ring. This and the fact that the cyclobutane ring is hexasubstituted may render it inaccessible to the platinum surface, effectively eliminating hydrogenolysis. The calculations suggest that rearrangement of (**3**) and (**5**) *via* expansion of the C$_4$ ring at the expense of



(3) (4) (5) (6)

(7) (8)

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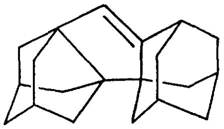
contracting a $C_6$ ring of one of the adamantyl groups is thermochemically favourable. Thus, expansion to a bridgehead position in (**3**) and (**5**) produces the noradamantyl structures (**7**) and (**8**) with a calculated strain release of 28·54 and 25·93 kcal mol$^{-1}$, respectively. An alternative possibility is that expansion of the $C_4$ ring proceeds to a non-bridghead carbon atom, producing a protoadamantane structure. $^{13}$C N.m.r. spectroscopy allows a distinction to be made: both (**3**) and (**5**) possess two quaternary carbon atoms and rearrangement leading to the noradamantane structures (**7**) and (**8**) introduces a third quaternary carbon atom whereas the protoadamantane alternative does not. The rearrangement products were separated by preparative g.l.c. and were assigned the structures (**7**) and (**8**) on $^{13}$C n.m.r. spectroscopic evidence for the presence of three quaternary carbon atoms in each. When the rearrangement was conducted in nitrogen at 210 °C, (**7**) and (**8**) were also produced together with an olefinic compound, *m/e* 266, which was assigned structure (**9**) on the evidence that catalytic hydrogenation converted it into (**8**).

TABLE[a]

| | (**3**) | (**4**) | (**5**) | (**6**) | (**7**) | (**8**) |
|---|---|---|---|---|---|---|
| $\Delta H^\circ_f$ | −3·02 | +14·65 | −6·97 | +18·52 | −32·67 | −34·01 |
| Strain energy | 66·16 | 83·83 | 62·21 | 87·70 | 37·62 | 36·28 |

[a] Gas phase data (25 °C) in kcal mol$^{-1}$.

The rearrangement of (**3**) and (**5**) into (**7**) and (**8**) represents the first example of the formation of a quaternary carbon atom with 100% selectivity on platinum (rearrangement was observed also on palladium with comparable results), and it shows clearly that an αα*λ*-triadsorbed intermediate is not required. An α*λ*-diadsorbed intermediate with transient formation and hydrogenolysis of a cyclopropane ring is obviously also ruled out. These results point to the intervention of a surface alkyl of type (**11**)‡ in which there is an antiperiplanar relationship between the carbon–metal bond and the migrating carbon–carbon bond; this stereochemical requirement is closely met since the force field calculations reveal a dihedral angle relationship in (**10**) of 172—173°.



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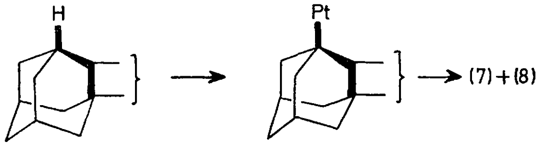

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‡ Deuterium–hydrogen exchange experiments give results consistent with the one-point attachment theory.

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