Gas-phase Reactions on Platinum. A Short Synthesis of Triamantane

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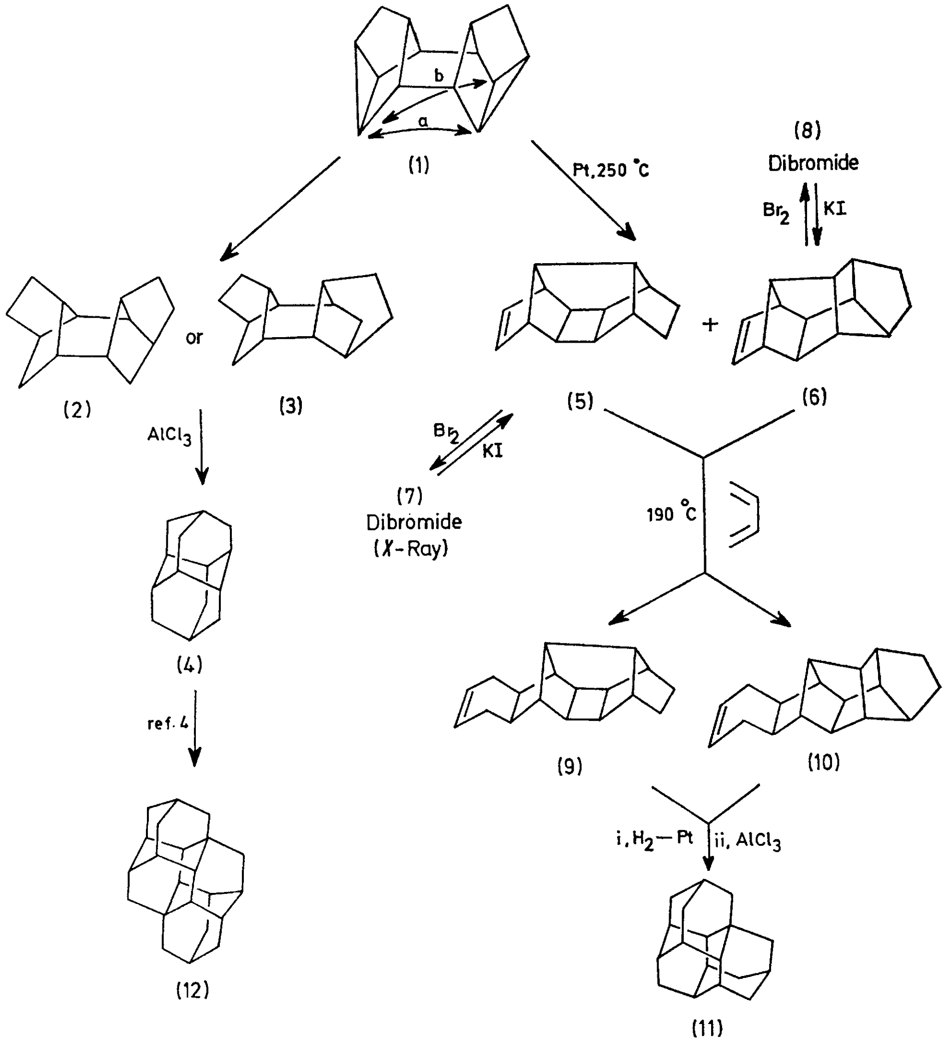
Summary Binor-S, the {4 + 4} dimer of norbornadiene, rearranges in the gas phase on a platinum catalyst and in solution with silver perchlorate, yielding two new norbornadiene dimers which can be elaborated in three steps into triamantane *via* {4 + 2} adducts with butadiene; the structure of one dimer has been established by an *X*-ray crystal analysis.

BINOR-S (**1**),[1] the readily accessible {4 + 4} dimer of norbornadiene, plays an important role in recent synthetic approaches to the larger diamondoid hydrocarbons, diamantane (**4**), triamantane (**11**), and *anti*-tetramantane (**12**). The cyclopropane rings are susceptible to hydrogenolytic opening on platinum under mild conditions; the resulting tetrahydro-derivative, of structure (**2**) or (**3**), rearranges into diamantane[2] on exposure to aluminium chloride and, as we have shown elsewhere, diamantane can be singly or doubly homologated into triamantane[3] or *anti*-tetramantane,[4] respectively. This route to triamantane comprised twelve stages, terminating in an unusual gas-phase olefin cyclisation on a platinum–silica catalyst. We now disclose a new feature of binor-S chemistry which makes triamantane available in four simple operations, commencing with another new gas-phase rearrangement on platinum.



SCHEME

X-Ray crystal analysis[5] of binor-S revealed that the *endo*-edges of the cyclopropane rings are held in close proximity, offering the possibility of opening one with concomitant involvement of the other. Ideally, we wished to replace

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both cyclopropane rings by one new carbon–carbon single bond along the direction indicated by *a* or *b* in (**1**) and one new carbon–carbon double bond since such an arrangement could then be elaborated to the C and H level appropriate to triamantane simply by adding butadiene in a {4 + 2} fashion and hydrogenating the adduct. The behaviour of binor-S on catalytic hydrogenation on platinum both in solution and in the gas phase showed that under these conditions the cyclopropane rings are cleaved essentially independently of each other. However, at elevated temperatures in the absence of hydrogen a quite different process occurred for when binor-S was vaporised in nitrogen and passed over 2% platinum on silica at 250 °C about equal amounts of two new liquid norbornadiene dimers, easily separable by spinning distillation, were obtained in good yield. Both products were $C_{14}H_{16}$ mono-olefins, though without cyclopropyl groups; accordingly, each must contain a new carbon–carbon single bond. ^{13}C N.m.r. spectroscopy suggested that one isomer was highly symmetrical (7 resonances) whereas the other was not (13 resonances). Both isomers formed crystalline adducts with silver nitrate and with bromine, the latter without rearrangement (see Scheme), and *X*-ray diffraction of the *trans*-dibromide (**7**) of the more symmetrical isomer revealed its structure to be (**5**).

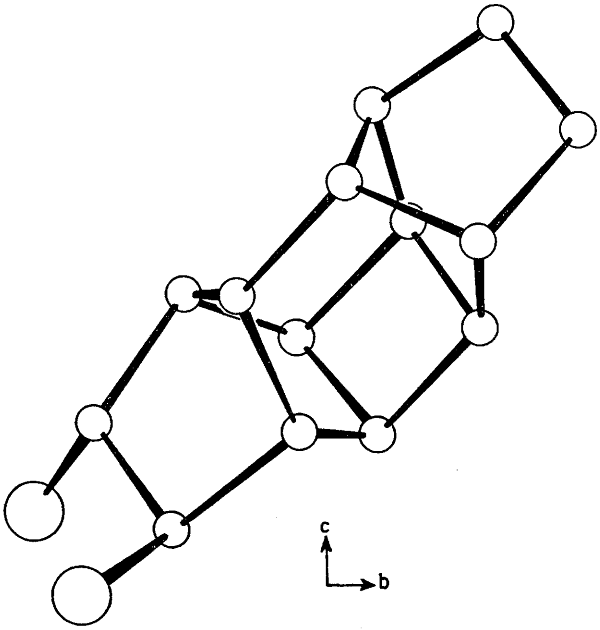

FIGURE. Projection of the molecule of (**7**) onto the *bc* plane.

Crystal data: (**7**); $C_{14}H_{16}Br_2$, monoclinic, space group $P2_1/c$, a = 10·98(5), b = 4·95(4), c = 7·66(2) Å, β = 96·5°, Z = 4. The structure was determined from 566 independent photographic intensities. Least-squares refinement of the structure with allowance for anisotropic vibration parameters for the two bromine atoms and isotropic vibrations for all carbon atoms gave R = 0·12. A projection of the molecule is shown in the Figure.

The olefin (**5**) is formally the product of a sequence commencing with fission of one cyclopropane ring of binor-S, probably *via* insertion of the metal into a carbon–carbon single bond, bond formation along direction *a* in (**1**) with opening of the second cyclopropane ring, and terminating in an elimination. We have not yet determined the structure of the second olefin; we suggest structure (**6**) on the grounds that bond formation along the direction indicated by *b* in (**1**) produces this result. Interestingly, olefins (**5**) and (**6**) were also produced (60%) from binor-S by the action of $AgClO_4$ in hot benzene.

The remaining stages were conducted using (**5**) and (**6**) separately or with *ca.* 1 : 1 mixtures of the two, with comparable results. A Diels–Alder reaction with butadiene at 180 °C furnished the crystalline adducts (**9**) and (**10**) (of undetermined stereochemistry) in high yield. Hydrogenation of the adducts removed the double bond and exposure of the dihydro-compounds to aluminium chloride in hot cyclohexane produced triamantane (**11**) in *ca.* 60% yield.

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