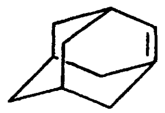
Adamantene and its Dimer

By D. Grant, M. A. McKervey,* J. J. Rooney, N. G. Samman, and G. Step
(*Department of Chemistry, The Queen's University, Belfast* BT9 5AG)

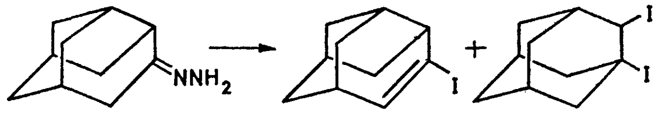
Summary Treatment of 1,2-di-iodoadamantane with n-butyl-lithium in pentane at 0° yields 98% of a $C_{20}H_{28}$ hydrocarbon which is formally the product of head-to-tail dimerisation of adamantene.

As suggested in the previous communication,[1] the ease with which palladium-catalysed deuterium–hydrogen exchange reactions propagate through the bridgehead positions of bridged-ring alkanes can be correlated with the stability of the appropriate bridgehead alkene, the absence of multiple exchange with adamantane reflecting the prohibitively large increase in strain energy which would accompany the formation of a π-complex of adamantene (**1**) with the metal. Wiseman and Pletcher[2] have made the useful proposal that the strain energies of bridged-ring alkenes in which one of the vinylic carbon atoms occupies a bridgehead position should be comparable with those of *trans*-cycloalkenes. On this basis, adamantene should be extremely unstable; there is no direct evidence for the existence of its monocyclic analogue, *trans*-cyclohexene.[3] However, bicyclo[2,2,1]hept-1(2)-ene, which also contains a *trans*-cyclohexene unit, appears to be an intermediate in the reaction of butyl-lithium with some dihalogenobicyclo[2,2,1]heptanes.[4] Evidence is here presented which suggests that the elusive adamantene (**1**) may be formed in the reaction of 1,2-di-iodoadamantane with n-butyl-lithium.[5]

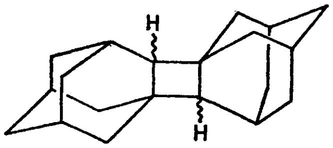
A cold solution of protoadamantan-4-one hydrazone (**2**) and triethylamine in chloroform was treated with iodine[6] in chloroform to yield 4-iodoprotoadamant-4-ene (**3**) (25%), b.p. 80—82° at 0·15 mmHg, and 1,2-di-iodoadamantane (**4**) (14%), m.p. 106—108°.† The iodo-olefin could be converted into the di-iodide quantitatively by treatment with hot hydriodic acid. Exposure of the di-iodide to n-butyl-lithium in pentane at 0° furnished a single dimeric hydrocarbon (98% isolated yield), $C_{20}H_{28}$, m.p. 152—153°, which has been assigned the head–tail adamantene dimer structure (**5**) on the following evidence. The absence of cyclopropyl or ethylenic functions was inferred from the spectral data and confirmed by the dimer's inertness towards Br_2–CCl_4, hot formic acid, and catalytic hydrogenation/hydrogenolysis in solution. Although simple cyclobutanes are susceptible to catalytic hydrogenolysis in the gas-phase at elevated temperatures, this was not the case with (**5**) at 220° in hydrogen on a platinum–silica catalyst; instead two new $C_{20}H_{28}$ hydrocarbons (ratio 2:1) were produced quantitatively. Use of rhodium–alumina or palladium–pumice at 200—220° gave essentially the same result. However, ring-opening was achieved *via* disproportionation: treatment of the dimer with aluminium trichloride in carbon disulphide at 20° for 1 h afforded predominantly (64%) a single $C_{20}H_{30}$ hydrocarbon, identified by combined g.l.c.–m.s. analysis as 1,2′-biadamantyl (**7**);[8] other products included a $C_{20}H_{26}$ hydrocarbon and the two $C_{20}H_{28}$ hydrocarbons obtained in the gas-phase reactions. We interpret the formation of (**7**) as evidence for the head–tail arrangement (**5**) rather than the head–head arrangement (**6**).



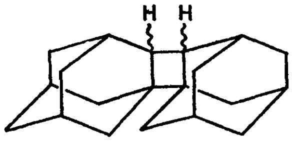
(**1**)



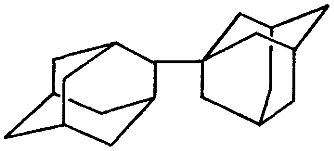
(**2**) (**3**) (**4**)



(**5**)



(**6**)



(**7**)

The remarkable propensity for rearrangement on catalysts with the dimer in the gas-phase (on palladium–pumice reaction was detectable at as low as 150°) is consistent with the presence of a cyclobutane ring. Models imply that (**5**) should be of very high strain energy since the torsion angles for cyclohexane are considerably larger than that for cyclobutane. This will substantially increase the cyclobutane torsion angle, and hence its strain energy, since the cyclohexane rings of the adamantane skeleton are rigidly interlocked and consequently much more difficult to deform. On the other hand, the bulky flanking adamantyl groups should render the cyclobutane ring inaccessible to a metal surface. Consequently, rearrangement on the metals, which probably initiates outside the four-membered ring, is favoured over hydrogenolysis. Although the rearrangement products have yet to be identified, they are most probably products of ring expansion of the cyclobutane ring since they were both stable towards hydrogen on platinum at 350°.

In the bis-dehalogenation of 1,2-dihalogenobicyclo[2,2,1]-heptanes, Keese and Krebs[4] found substantial amounts of unidentified $C_{14}H_{20}$ hydrocarbons. On the basis of our work, these products are almost certainly cyclobutane-containing dimers. They also obtained Diels–Alder adducts with

---

† Satisfactory analytical and spectral data were obtained.

furan, thereby providing compelling evidence for the intermediacy of bicyclo[2,2,1]hept-1(2)-ene. Thus far we have been unable to trap adamantene in a Diels–Alder reaction, but this need not necessarily imply that adamantene is not produced from the di-iodide. An alternative explanation is that adamantene is so much more highly twisted about the double bond axis than is bicyclo[2,2,1]hept-1(2)-ene that it is in fact unreactive as a dieneophile compared with its reactivity in dimerisation; the extreme double bond twist and the concomitant twisting of the orbitals provide to a high degree the precise requirements for a symmetry-allowed dimerisation.[9] The stereochemistry of (**5**), which is of interest in relation to the stereochemistry of $[_{\pi}2_a + {}_{\pi}2_s]$ combinations, is under investigation.

We thank the Shell Chemical Company for financial support.

(*Received*, *7th August* 1972; *Com.* 1392.)

---

[1] M. A. McKervey, J. J. Rooney, and N. G. Samman, preceding communication.

[2] J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 1970, **92**, 956.

[3] The intermediacy of *trans*-cyclohexene in photolysis of *cis*-cyclohexene has been postulated, J. A. Marshall, *Accounts Chem. Res.*, 1969, **2**, 33.

[4] R. Keese and E. P. Krebs, *Angew. Chem. Internat. Edn.*, 1971, **10**, 262; *ibid.*, 1972, **11**, 518.

[5] An unsuccessful attempt to produce adamantene photolytically by Norrish type II elimination of adamantan-1-ylacetone has been described by R. G. Gagosian, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 4752.

[6] *Cf.* D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 1962, 470.

[7] For a recent discussion and leading references see G. Maire and F. G. Gault, *Bull. Soc. chim. France.*, 1967, 894.

[8] This compound was first prepared by aluminium chloride-catalysed addition of adamantane to 2,4-dehydroadamantane, see H. J. Storesund, *Tetrahedron Letters*, 1971, 4353. The material used in the present work for comparative purposes was prepared by coupling an equimolar mixture of 1- and 2-bromoadamantane using sodium in xylene; the product was a 1:6:3 mixture of 1,1′-, 2,2′-, and 1,2′-biadamantyl; *cf.* H. Reinhardt, *J. Org. Chem.*, 1968, **27**, 3258.

[9] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, 1970, p. 75.