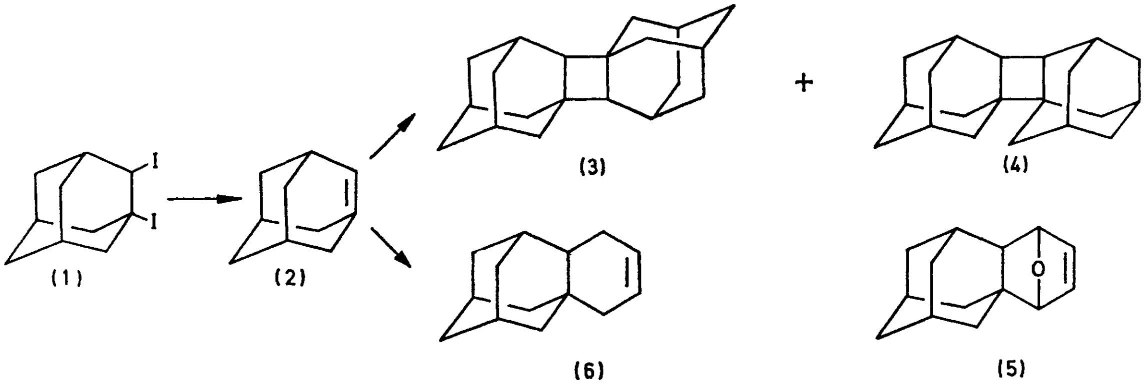
The Existence of Adamantene

By WILLIAM BURNS and M. ANTHONY MCKERVEY*
(*Department of Chemistry, The Queen's University, Belfast* BT9 5AG)

Summary Reaction of 1,2-di-iodoadamantane with n-butyllithium yields adamantene which can be trapped in a Diels-Alder reaction with butadiene at −80°.

ON exposure to Bu^nLi, 1,2-di-iodoadamantane (**1**) yields two dimeric hydrocarbons (**3**) and (**4**)[1,2] and it has been suggested that this dehalogenation reaction proceeds *via* the transient formation of the highly strained bridgehead olefin adamantene (**2**) which dimerises spontaneously in a 2 + 2 fashion. This interpretation has been questioned by Wynberg and his co-workers[3] on the grounds that if adamantene is indeed capable of existence it should be susceptible to interception in a Diels–Alder reaction, but when the dehalogenation was conducted in the presence of furan the expected adduct (**5**) was not detected among the products. It is possible, however, that because of the extreme torsional distortion of the double bond, adamantene may react more readily in a ${}_{\pi}2_{s} + {}_{\pi}2_{a}$ cycloaddition than in a (supra–supra) 4 + 2 reaction. Furthermore, furan may have been a poor choice as the trapping agent: a Dreiding model of adduct (**5**) reveals much torsional strain about the conjoining bonds, indicating that the molecule should have a very high strain energy. The latter problem should not arise with an acyclic diene–adamantene adduct.



Treatment of the di-iodide (**1**) with $Bu^{n}Li$ in ether–pentane containing a large excess of butadiene at −80° gave, in addition to much polymer, *ca.* 15% of a new substance having a g.l.c. retention time (silicon gum rubber) appreciably shorter than that of the dimers which were still the major products of the reaction (*ca.* 85%). The minor product reacted with Br_2 in CCl_4 and it was isolated from the reaction mixture as a crystalline dibromide (M^+ 346, 348, 350) and re-formed with KI in hot MeOH. The olefin was obtained as an oil and its molecular weight by mass spectrometry (found 188·1560; calculated 188·1559) and n.m.r. spectrum [δ 0·9—2·2 (18H) and 5·65 (2H)] were consistent with the butadiene-adamantene adduct (**6**). This, we suggest, provides compelling evidence for the existence of adamantene.[4]

We thank the Department of Education for a postgraduate grant to W.B.

(*Received*, 12*th August* 1974; *Com.* 1030.)

---

[1] D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J.C.S. Chem. Comm.*, 1972, 1186.

[2] D. Lenoir, *Tetrahedron Letters*, 1972, 4049; D. Lenoir and J. Firl, *Annalen*, in the press. We thank Dr. Lenoir for informing us that adamantene dimer is a 2 : 1 mixture of isomers (**3**) and (**4**).

[3] A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Letters*, 1973, 3047.

[4] Photochemically generated adamantene has been claimed by J. E. Gano and L. Eizenberg, *J. Amer. Chem. Soc.*, 1973, **95**, 972.