

Non-coplanar Double Bonds; The Existence of Adamantene

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On exposure to n-butyl-lithium, 1,2-di-iodoadamantane yields the highly strained bridgehead olefin adamantene, which can be intercepted in a Diels–Alder reaction with butadiene at $-78\text{ }^{\circ}\text{C}$; in the absence of butadiene it dimerises spontaneously in a [2 + 2] fashion.

OF the various statements of the amount of distortion an olefin can sustain and still constitute an isolable substance, much historical interest attaches to that of Bredt,¹ who postulated that compounds of the pinane and camphane class cannot have a double bond at a bridgehead position. Bredt's rule represents the first qualitative expression of the limits to the amount of torsional strain an olefin can tolerate. The consequences of this type of distortion in which the $2p$ orbitals of the π -bond are skewed relative to each other by an amount proportional to the twist of the π -bond have received much scrutiny, and there have been several attempts to probe the limits of Bredt's rule.² *trans*-Cyclo-octene (1)³ provides an illustration of one way of imposing torsional strain in an olefin: the methylene chain linking the *trans*-substituents in pro-

jection (2) is of insufficient length to permit complete overlap of the p -orbitals. Better overlap is attained if the vinylic carbon atoms undergo slight rehybridisation, as in (3), with incorporation of some s character into the lobes of the π -bond, and this type of compromise appears to be quite general in strained olefins.⁴ A second, closely related way of imposing torsional strain is to place the double bond at a bridgehead position of a bicyclic system, as in bicyclo[3.3.1]non-1-ene (4).^{5,6} Olefins (1) and (4) are highly reactive, though isolable substances, and a feature common to both is the presence of a *trans*-double bond in an eight-membered carbocycle. These similarities led Wiseman to elaborate Bredt's rule to include a comparison of the strain energies of *trans*-monocycloalkenes with those of the corresponding bicyclic bridgehead alkenes. Thus, *trans*-cycloheptene⁷ and its bi-

¹ J. Bredt, H. Thouet, and J. Schmitz, *Annalen*, 1924, **437**, 1.
² For a recent review of Bredt's rule see G. L. Buchanan, *Chem. Soc. Rev.*, 1974, **3**, 41.

³ K. Ziegler and H. Wilms, *Annalen*, 1950, **567**, 1.

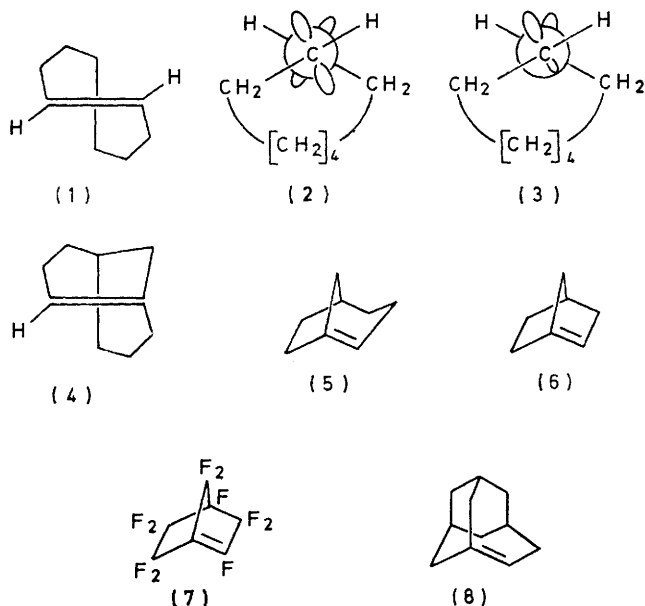
⁴ Cf. N. L. Allinger, *J. Amer. Chem. Soc.*, 1958, **80**, 1953; W. L. Mock, *Tetrahedron Letters*, 1972, 475.

⁵ J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 1970, **92**, 956.

⁶ J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 1970, **92**, 948.

⁷ E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934.

cyclic analogue (5)⁸ can exist, but cannot be isolated. The extension of this analogy to the six-membered series is of particular interest since there is no direct evidence for the existence of *trans*-cyclohexene.* However, the *trans*-cyclohexene analogues bicyclo[2.2.1]hept-1-ene (6)¹⁰ and perfluorobicyclo[2.2.1]hept-1-ene (7)¹¹ have been trapped in a Diels–Alder reaction with furan.



Bredt's rule relates specifically to bridgehead double bonds in bicyclic systems. Bridged-ring tricyclic systems of comparable size are much more rigid, the distortion and excess strain produced by a bridgehead double bond should be much more severe, and there are insufficient data available to establish whether or not Wiseman's modification of Bredt's rule applies to such systems. The observation of homoadamantene (8), the tricyclic analogue of *trans*-cycloheptene has recently been claimed; it dimerises spontaneously.^{12,13} Adamantene (9), the tricyclic analogue of *trans*-cyclohexene, represents a much more extreme case of a highly inflexible system in which

* The intermediacy of *trans*-cyclohexene in photolysis of *cis*-cyclohexene has been postulated.⁹

† After the publication of a preliminary account of this work,¹⁶ Dr. D. Lenoir, who was independently pursuing the same objective,¹⁶ kindly informed us of a superior route to the di-iodide, involving the reaction of protoadamantan-4-one with neat phosphorus tri-iodide.¹⁷ In subsequent work we adopted this alternative with the slight modification that the reaction was conducted in hot chloroform whereupon a 92% yield of the di-iodide was obtained.

‡ Although simple cyclobutanes are susceptible to catalytic hydrogenolysis in the gas phase at elevated temperatures,¹⁸ this was not the case with the cyclobutanes (13) and (14) at 220 °C in hydrogen on a platinum–silica catalyst; instead two new C₂₀H₂₈ hydrocarbons (ratio 2 : 1) were produced quantitatively. Use of rhodium–alumina or palladium–pumice at 200–220 °C gave essentially the same results. The structures of these rearrangement products, which correspond in their g.l.c. retention times with two of the minor products of the aluminium trichloride reaction, are under investigation (work in progress with Dr. J. J. Rooney).

the opportunity for distributing the large angle strain over several bonds is at a minimum. Nevertheless, adamantene can exist, though it cannot be isolated, as we now illustrate.

The synthetic route chosen involved dehalogenation of a 1,2-dihalogenoadamantane with an alkyl-lithium. Treatment of a cold solution of protoadamantan-4-one hydrazone (10) and triethylamine in chloroform with iodine¹⁴ yielded a separable mixture of 1,2-di-iodoadamantane (11) (14%)[†] and 4-iodoprotoadamant-4-ene (12) (25%). The structural assignments are based on analytical and spectral data (see Experimental section), the mode of formation, and the observation that exposure of the iodo-olefin to hot hydriodic acid gave the di-iodide in 91% yield. Treatment of the di-iodide with *n*-butyl-lithium in pentane at 0 °C furnished, in essentially quantitative yield, a C₂₀H₂₈ hydrocarbon, m.p. 151–153°, which originally¹⁵ was believed to be the head-to-tail adamantane dimer (13), exclusively on the grounds that upon exposure to aluminium trichloride in carbon disulphide it underwent ring opening *via* disproportionation, yielding a single C₂₀H₃₀ hydrocarbon (64%) identified as 1,2'-biadamantyl (15) by g.l.c.–mass spectrometry; neither 1,1'- nor 2,2'-biadamantyl was detected but other unidentified products included a C₂₀H₂₈ hydrocarbon and two C₂₀H₂₈ hydrocarbons (*ca.* 30% total). We interpreted the exclusive formation of (15) as evidence for the head-to-tail arrangement (13) rather than the head-to-head arrangement (14). More recently, however, Lenoir and Firl¹⁷ have shown by high resolution g.l.c. that adamantene dimer is a 2 : 1 mixture of (13) and (14) and from ¹³C n.m.r. analysis have assigned the *cis*-arrangement to (13) and the *trans*-arrangement to (14). Clearly the isomers (13) and (14) differ in their mode of reaction with aluminium trichloride in carbon disulphide.‡

Although the formation of [2 + 2] dimers in the dehalogenation of the di-iodide (11) suggests the intervention of adamantene, we sought more compelling evidence and attempted to trap the intermediate in a Diels–Alder reaction. Experiments with a large excess of furan in the reaction mixture were uniformly unsuccessful; the expected adduct (16) was not detected, though the dimers were formed as usual. This failure with furan prompted

⁸ J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, 1969, **91**, 7775.

⁹ J. A. Marshall, *Accounts Chem. Res.*, 1969, **2**, 22.

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

¹¹ S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1965, **21**, 3008.

¹² M. Farcasiu, D. Farcasiu, R. T. Conlin, M. Jones, jun., and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8207.

¹³ B. L. Adams and P. Kovacic, *J. Amer. Chem. Soc.*, 1973, **95**, 8206.

¹⁴ Cf. D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 1962, 470.

¹⁵ D. Grant, M. A. McKerverey, J. J. Rooney, N. G. Samman, and G. Step, *J.C.S. Chem. Comm.*, 1972, 1186.

¹⁶ D. Lenoir, *Tetrahedron Letters*, 1972, 4049.

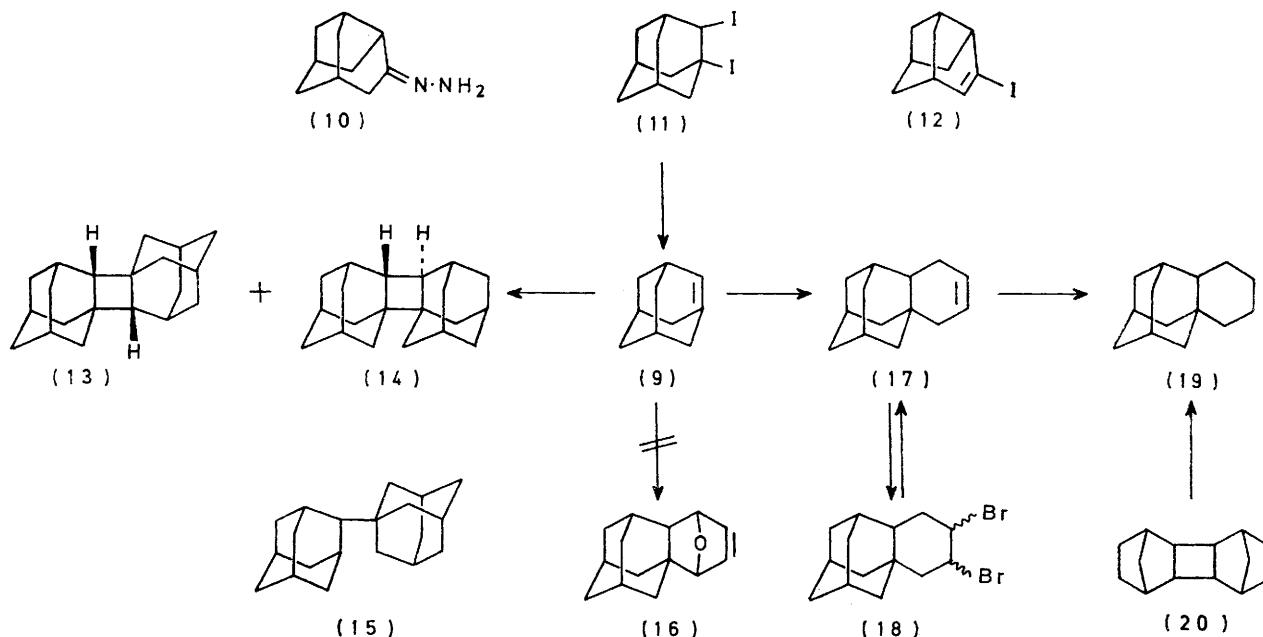
¹⁷ D. Lenoir and J. Firl, *Annalen*, 1974, 1467.

¹⁸ For a recent discussion and leading references see G. Maire and F. G. Gault, *Bull. Soc. chim. France*, 1967, 894.

Wynberg and his co-workers¹⁹ to suggest that adamantene is not a transient intermediate in the dehalogenation of the di-iodide on the grounds that such a highly reactive olefin should surely be capable of interception by furan; they also suggested that the dimers are formed *via* a stepwise coupling process. None of this is necessarily true. In the first place, adamantene should possess a very large torsion angle about the double bond and, as Woodward and Hoffmann²⁰ have pointed out, the concomitant twisting of the orbitals of such an olefin provides to a high degree the precise requirements for a

the new substance. In this modification the insolubility of the di-iodide causes adamantene to be generated at very low concentration, and dimerisation is thereby suppressed in favour of capture by butadiene. Much of the polymerisation was later traced to the work-up procedure; and when this was modified by adding water to the reaction mixture at -78°C and pumping off the excess of butadiene at reduced pressure, the extent of polymerisation was greatly reduced.

The new substance reacted with bromine and it was isolated from the reaction mixture as a crystalline



symmetry-allowed dimerisation; in other words, adamantene should be especially prone to dimerisation. Secondly, furan may have been a poor choice as trapping agent: a Dreiding model of the adduct (16) reveals much torsional distortion about the conjoining bonds, suggesting that the molecule should have a very high strain energy. The latter problem should not arise with an acyclic diene-adamantene adduct. And indeed when a *solution* of the di-iodide in ether-pentane containing a large excess of butadiene at -78°C was treated with *n*-butyllithium we obtained, in addition to much polymer, *ca.* 15% of a new substance having a g.l.c. retention time appreciably shorter than that of the dimers which were still the major products (*ca.* 85%) of the reaction.²¹ A simple modification of this procedure completely changed the product ratio, for when a *suspension* of the di-iodide in neat butadiene at -78°C (ether having been used in the previous experiment to bring it into solution) was similarly treated, the product ratio was 85 : 15 in favour of

dibromide (18) (M^+ 346/348/350) and regenerated with potassium iodide in hot dry methanol. The liquid olefin (17) was obtained in 67% yield and its molecular weight by mass spectrometry and n.m.r. spectrum were consistent with the butadiene-adamantene adduct structure (17). This assignment could be substantiated as follows. It is known that on exposure to aluminium bromide the hydrocarbon (20) (a mixture of stereoisomers) undergoes rearrangement accompanied by disproportionation, yielding as the major product, 1,2-tetramethyleneadamantane (19).²² We repeated this preparation, isolated (19) by preparative g.l.c. and found it identical with the product of hydrogenation of the butadiene-adamantene adduct (17).

This work provides compelling evidence for the existence of an unstable intermediate in the dehalogenation of 1,2-di-iodoadamantane, which behaves as if it were the olefin adamantene (9). More recently, the observation of adamantene has been claimed by two other groups.

¹⁹ A. H. Alberts, J. Strating and H. Wynberg, *Tetrahedron Letters*, 1973, 3047.

²⁰ R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970, p. 75.

²¹ W. Burns and M. A. McKervey, *J.C.S. Chem. Comm.*, 1974, 858.

²² T. M. Gund, E. Osawa, V. Z. Williams, jun., and P. von R. Schleyer, *J. Org. Chem.*, 1974, **39**, 2979.

Gano and Eizenberg²³ found that photochemical Norrish type II fragmentation of either 1- or 2-adamantyl phenylacetate in methanol yielded 1-methoxyadamantane, suggesting the intervention of adamantene, and Alberts *et al.*¹⁹ obtained a trace of an adduct with 2,5-dimethylfuran in the thermolysis of an adamantane-1,2-diylbisperoxy-ester. Surprisingly, no dimers were formed in the latter approach.

EXPERIMENTAL

M.p.s were determined for samples sealed in capillary tubes. Unless otherwise stated i.r. spectral data relate to dispersions in potassium bromide discs. ¹H N.m.r. data were measured at 60 MHz with tetramethylsilane as internal standard. Mass spectrometric data were obtained with an A.E.I. MS 902 instrument and with an A.E.I. MS 30 instrument attached to a Pye-Unicam series 104 gas chromatograph. Differential thermal analysis (d.t.a.) was performed on a Dupont 900 thermal analyser fitted with a d.s.c. cell. G.l.c. refers to analysis on one of the following columns: (A) 2 m Silicone Gum Rubber on Chromosorb W (5% w/w); (B) 20 m Apiezon L capillary. Preparative g.l.c. was performed on a 10 ft × $\frac{3}{8}$ in column of Silicone Gum Rubber on Chromosorb W (30% w/w). Spence type H alumina and Whatman SG 31 silica gel were used for adsorption chromatography. Light petroleum had b.p. 40–60°. The drying agent employed was magnesium sulphate.

Protoadamantan-4-one.—The ketone was prepared in 65% yield from adamantane-1-ol according to the published procedure.²⁴

Protoadamantan-4-one Hydrazone (10).—Protoadamantan-4-one (5.0 g) in ethanolic 10% potassium hydroxide (70 ml) was treated with 98% hydrazine (15 ml). The solution was heated under reflux for 1 h, then cooled, poured into cold water (250 ml), and extracted with ether (4 × 50 ml). The extract was washed with water, dried, and concentrated, yielding a waxy solid (5.5 g). I.r. and mass spectral analysis indicated that the product was a mixture of the hydrazone (10) and the corresponding azine. Attempts to isolate the hydrazone by crystallisation of the mixture from ethanol, aqueous ethanol, benzene, xylene, or hexane led to complete conversion into the azine. Accordingly, the mixture was used directly in the following experiment.

4-Iodoprotadamant-4-ene (12) and *1,2-Di-iodo-adamantane* (11).—The crude hydrazone (5.2 g) was dissolved in dry benzene (95 ml) and dry triethylamine (11.1 ml) was added. The solution was stirred under nitrogen at room temperature while a solution of iodine (10.0 g) in dry benzene (100 ml) was added dropwise over 2 h. After nitrogen evolution had ceased the mixture was stirred for a further 2 h, then washed successively with *N*-hydrochloric acid, water, saturated aqueous sodium hydrogen carbonate, and water. The solution was dried and concentrated, yielding an oil which was placed on a column of alumina (1 kg). Elution with benzene gave the *iodo-olefin* (12) (2.0 g, 25%), b.p. 80° at 0.1 mmHg (Found: C, 46.5; H, 5.15; I, 48.25%; *M*⁺, 260.0064. C₁₀H₁₄I requires C, 46.15; H, 5.05; I, 48.8%; *M*, 260.0064, τ (CDCl₃) 3.20–3.32 (1 H, d, vinylic) and 7.9–8.6 (12 H, m), *m/e* 260 (15%, *M*⁺), 135 (15), 133 (16), 105 (10), 91 (100),

79 (16), and 67 (12). Further elution with benzene gave the *di-iodide* (11) (1.7 g, 14%), m.p. 106–108° (Found: C, 31.3; H, 3.7%; *M*⁺, 387.9186. C₁₀H₁₄I₂ requires C, 30.95; H, 3.65; I, 65.4%; *M*, 387.9188), τ (CDCl₃) 4.91 (1 H, s) and 7.15–8.5 (13 H, m), *m/e* 388 (11%, *M*⁺), 261 (100), 134 (44), 105 (20), 91 (59), 79 (38), 77 (28), and 67 (19). Further elution with light petroleum–ether (3:1) gave some protoadamantan-4-one.

Reaction of the Iodo-olefin (12) with *Hydriodic Acid*.—A mixture of the iodo-olefin (2.4 g) and constant-boiling hydriodic acid (40 ml) was heated under reflux for 3 h, then cooled, poured into water (100 ml), and extracted with chloroform (4 × 50 ml). The extract was washed with water, aqueous sodium thiosulphate, and water, and dried. Removal of the solvent gave the di-iodide (11) (3.4 g, 91%).

Reaction of Protoadamantan-4-one with Phosphorus Tri-iodide.—To a solution of iodine (450 g) in chloroform (2.4 l) was added red phosphorus (53 g) with stirring. The mixture was stirred at room temperature for 1½ h, a solution of protoadamantan-4-one (19.2 g) in chloroform (100 ml), was added, and the resulting mixture was heated to 55 °C for 5 h. After cooling, the solution was poured into water (3 l) and filtered. The organic layer and dichloromethane extracts (3 × 150 ml) of the aqueous layer were combined, washed with aqueous sodium thiosulphate and water, then dried. Removal of the solvent gave a pale yellow solid (47.2 g) which was placed on a column of silica gel (1.3 kg). Elution with light petroleum–ether (9:1) gave the di-iodide (11) (45.4 g, 92%), identified by direct comparison with the material described above.

Reaction of the Di-iodide (11) with *n*-Butyl-lithium.—*n*-Butyl-lithium [22 ml of a 23.1% (w/w) solution in hexane] was added dropwise with stirring to a solution of the di-iodide (11) (3.6 g) in pentane under nitrogen at 0 °C. The solution was stirred for a further 3 h and water (150 ml) was added. The organic layer and ethereal extracts (3 × 50 ml) of the aqueous layer were combined, washed with water, and dried. Removal of the solvent gave a semi-solid which was placed on a column of alumina. Elution with pentane gave the adamantene dimers (13) and (14) (1.3 g, 100%). Crystallisation from hexane–methanol gave prisms, m.p. 151–152° (Found: C, 89.4; H, 10.75%; *M*⁺, 268.2191. Calc. for C₂₀H₂₈: C, 89.5; H, 10.5%; *M*, 268.2191), τ (CDCl₃) 7.8–8.8 (complex), *m/e* 268 (100% *M*⁺), 225 (33), 211 (13), 135 (26), 91 (28), 79 (24), 77 (12), and 67 (12). G.l.c. analysis on columns (A) and (B) showed a single peak for dimers (13) and (14). D.t.a. showed only one endotherm at 152 °C.

Reaction of the Dimers (13) and (14) with *Aluminium Chloride*.—Aluminium chloride (0.2 g) was slurried in dry carbon disulphide (100 ml) at room temperature and a solution of the dimers (0.2 g) in carbon disulphide (100 ml) was added. The mixture was stirred for 1 h then poured onto ice–water. The organic layer and carbon disulphide extracts of the aqueous layer (2 × 50 ml) were combined, washed with water, and dried. Removal of the solvent yielded a semi-crystalline solid (0.19 g, 93%) which was shown by g.l.c. analysis on columns (A) and (B) at 200 °C to be a mixture of 1,2'-biadamantyl (15) (64%), an unidentified hydrocarbon of molecular weight 266, and two unidentified hydrocarbons of molecular weight 268 (total 36%). Co-injection with authentic samples of 1,1'-biadamantyl and 2,2'-biadamantyl established that these compounds were not

²³ J. E. Gano and L. Eisenberg, *J. Amer. Chem. Soc.*, 1973, **95**, 972.

²⁴ W. H. W. Lunn, *J. Chem. Soc. (C)*, 1970, 2124; R. M. Black and G. B. Gill, *Chem. Comm.*, 1970, 972.

among the products. Preparative g.l.c. of the crude product gave 1,2'-biadamantyl (15) as needles, m.p. 263 (lit.,²⁵ 266—268°), identical with a sample prepared by Wurtz coupling between 1- and 2-bromoadamantane with sodium in toluene.

Reaction of the Di-iodide (11) with n-Butyl-lithium in Liquid Butadiene.—To a suspension of the di-iodide (7.0 g) in dry butadiene (250 ml) at -78°C under nitrogen was added dropwise with stirring n-butyl-lithium in hexane (23.1% w/w; 50 ml), and the mixture was then stirred at -78°C for 15 h. Water (50 ml) was added dropwise and the mixture was allowed to warm to -40°C . The flask was connected to a water aspirator and the excess of butadiene was removed by pumping at -40°C . Ether (150 ml) and water (250 ml) were added to the residue and the ether layer and ethereal extracts of the aqueous layer (3×100 ml) were combined, washed with water, and dried. Removal of the solvent gave an oil (10.8 g). G.l.c. analysis on column (A) at 215°C revealed the presence of dimers and a new shorter-retention-time component in the ratio *ca.* 1 : 15. Combined g.l.c.-mass spectrometric analysis established that the major component had M^+ 188, indicative of an adamantene-butadiene adduct.

Isolation of the Adamantene-Butadiene Adduct (17).—The crude product from the previous experiment was taken up in chloroform and 10% bromine in chloroform was added dropwise with stirring until the red colour persisted. The solution was washed with aqueous sodium disulphite and water, and dried. Removal of the solvent gave a viscous oil (19.8 g), g.l.c. analysis of which on column (A) at 215°C revealed the disappearance of the adduct (17). The product was placed on a column of silica gel (700 g). Elution with light petroleum gave the dimers (13) and (14) (0.3 g, 13%). Further elution with light petroleum-ether (99 : 1) gave the dibromide (18) (9.3 g) as an oil which slowly crystallised.

A sample crystallised from hexane had m.p. 92—94° (Found: C, 48.25; H, 5.85; Br, 45.9. Calc. for $\text{C}_{14}\text{H}_{20}\text{Br}_2$: C, 48.3; H, 5.8; Br, 45.9%), τ (CDCl_3) 7.5—8.8 (12 H, m), and 5.4—6.0 (2 H, m), M^+ 350/348/346.

The crude product was taken up in dry methanol (300 ml) containing potassium iodide (60 g) and the solution was heated under reflux for 48 h. The cooled solution was diluted with water (1.5 l) and extracted with dichloromethane (5×200 ml). The extracts were washed with aqueous sodium thiosulphate and water, then dried. Removal of the solvent gave an oil, g.l.c. analysis of which on column (A) at 215°C revealed the absence of the dibromide and the presence of a single component having a retention time identical with that of the adduct (17). The product was passed through a column of alumina (300 g) in light petroleum, yielding *tricyclo*[7.3.1.1^{7,11}.0^{1,6}]tetradec-3-ene as an oil (2.28 g, 67%). A sample obtained by preparative g.l.c. at 215°C (Found: C, 89.45; H, 10.7%; M^+ , 188.1560. $\text{C}_{14}\text{H}_{20}$ requires C, 89.3; H, 10.7%; M , 188.1559) showed τ (CDCl_3) 9.1—7.8 (18 H) and 4.35 (2 H), m/e 188 (100%, M^+) 131 (38), 91 (22), 79 (20), and 67 (10).

Hydrogenation of the Adduct (17).—The olefin (17) (0.184 g) in methanol (80 ml) containing Adams' catalyst (0.25 g) was exposed to hydrogen at 1 atm and room temperature. When uptake had ceased the catalyst was removed and the filtrate concentrated, yielding the hydrocarbon (19) (0.186 g) as an oil. A sample obtained by preparative g.l.c. at 215°C was identical (g.l.c.; mass and n.m.r. spectra) with a sample prepared by aluminium bromide-catalysed rearrangement-disproportionation of the hydrogenated norbornadiene dimer (20).²²

We thank the Northern Ireland Department of Education for a postgraduate award (to W. B.).

²⁵ H. J. Storesund, *Tetrahedron Letters*, 1971, 4353.