

SYNTHESIS AND STRUCTURE ANALYSIS OF 2,4,6,9-TETRADEHYDROADAMANTANE, (PENTACYCLO[4.4.0.0², 10.0³, 5.0⁴, 8]DECANE), A NOVEL STRAINED POLYCYCLIC HYDROCARBON¹

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Abstract—Thermolysis of the di-lithium salt of 2,6-adamantanedione bis-tosylhydrazone (II) gives a mixture of three volatile C₁₀H₁₂ hydrocarbons. The structure of two of these has been elucidated by spectroscopy and established as 2-methylenebicyclo[3.3.1]nona-3,6-diene (III) and 2,4,6,9-tetrahydroadamantane (IV). Catalytic hydrogenation of IV gives 2,4-dehydroadamantane (VII) and tetracyclo[4.4.0.0², 10.0⁴, 8]decane (VIII). Compound IV has no tendency for isomerization by silver ions either thermally or catalytically.

INTRODUCTION

In the adamantane series there are two instances of strained dehydroderivatives, each containing one C—C bond more than the parent compound, in such a way that a cyclopropane ring is incorporated.^{2,3} We were intrigued by the possibility of introducing two extra C—C bonds, formally leading to a tetrahydroadamantane, representing a novel, presumably highly-strained, polycyclic system.

An attractive route to tetrahydroadamantane is intramolecular carbene insertion, generated by alkaline decomposition of an adamantanedione bis-tosylhydrazone.⁴ To favour an *intramolecular* insertion reaction, thermolysis of the dry lithium salt of the tosylhydrazone was carried out.⁵ Since double bond formation in the adamantane skeleton is supposed to be highly improbable⁶ the formation of two cyclopropane rings is feasible, provided that no fragmentation or rearrangement occurs.

RESULTS AND DISCUSSION

2,6-Adamantanedione (I),⁷ obtained from adamantane by reaction with 20% oleum followed by chromic acid oxidation,⁸ was converted into the di-lithium salt of the bis-tosylhydrazone (II) by conventional methods (Fig. 1).

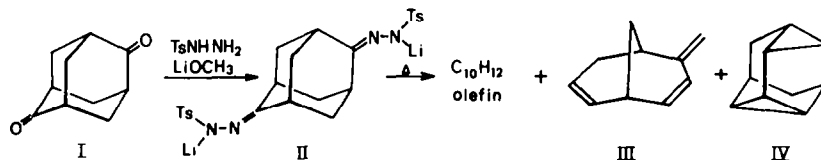


FIG. 1.

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Thermolysis of II (2–3 g scale) *in vacuo* led to a violent reaction commencing suddenly at about 155°. The vapours produced were condensed on a separate cold finger. The reaction could be moderated by diluting II with an equal weight of glass powder, but this did not improve the yield of condensed products.

The colourless condensate, which, for the greater part often solidified, proved by GLC analysis to consist of a mixture of three volatile components and minor amounts of less volatile products. The three volatile compounds were isolated by prep GLC. * Two of these were obtained as liquids, the third was a solid, yields after isolation being 3, 9, and 12%, respectively, based on 2,6-adamantanedione. Appreciable material loss was due to the high volatility of the substances.

Mass spectra† revealed that all three compounds had the molecular formula $C_{10}H_{12}$. Surprisingly, the three spectra were identical except small differences in signal intensities. Apparently all three components rearrange to the same or very similar parent ions upon ionization. Thus further information could not be obtained from these mass spectra.

The first component (liquid) proved to be an olefin as several olefinic hydrogens were detected by 1H NMR spectroscopy.‡ The substance exhibited a strong tendency to polymerize. The polymerization had already started in the condensing tube, as was noticed by the gradual decrease in time of the GLC peak area of this component. Despite attempts to inhibit polymerization we did not succeed in collecting sufficient quantity of monomer pure enough for a satisfactory structure analysis.

The second, component (liquid) was also an olefine. Its structure was established as 2-methylenebicyclo[3.3.1]nona-3,6-diene (III) as follows. The IR spectrum § (CCl_4) showed characteristic bands at 3060 ($C=CH_2$), 1586 and 1622 ($C=C$, conj.), and 882 cm^{-1} ($C=CH_2$). The UV spectrum § (cyclohexane) showed an absorption band at 249 nm with $\epsilon = 8800$ indicating the conjugation of two double bonds. The 1H NMR spectrum (CCl_4) showed six olefinic hydrogens suggesting at least three double bonds. In accordance with the molecular formula of $C_{10}H_{12}$ (from MS) we must have a bicyclic system. The detailed structure was determined by 1H NMR (100 MHz) with spin decoupling (Table 1).

The third component was a solid (m.p. 152–154°). It did not absorb UV light above 220 nm and from both IR and Laser-Raman spectra|| there were no indications of insaturation. The 1H NMR spectrum showed proton signals only below δ 2.8. In agreement with the molecular formula of $C_{10}H_{12}$ (from MS and elemental analysis)¶ this compound must be pentacyclic.

* Analytical as well as prep GLC was carried out with a Varian Aerograph, series 2000, operating at 100°, using 2 m columns with 4 or 6 mm ϕ , packed with Chromosorb Waw, silanized, and impregnated with Apiezon L (10%) and Carbowax 20M (1%); carrier gas helium or hydrogen (TC-detector).

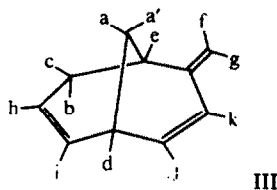
† Mass spectra were obtained from a AEI-MS 9 spectrometer by W. J. Rooselaar and N.M.M. Nibbering, this laboratory (direct probe insertion and heated inlet insertion gave identical spectra).

‡ 1H NMR spectra were recorded on a Varian HA 100 by K. Spaargaren, this laboratory, or G. Breman, N.V. Philips-Duphar. F. W. van Deursen gave helpful information for the interpretation of the spectra.

§ UV spectra were measured on a Cary 14, IR spectra on a Unicam SP 200, by C. Kruk, this laboratory.

|| A powder Raman spectrum was kindly recorded by Dr. C. Altona, Chemical Laboratories, University of Leiden, The Netherlands, on a Cary 81 Raman spectrophotometer; excitation with a Helium-Neon Laser.

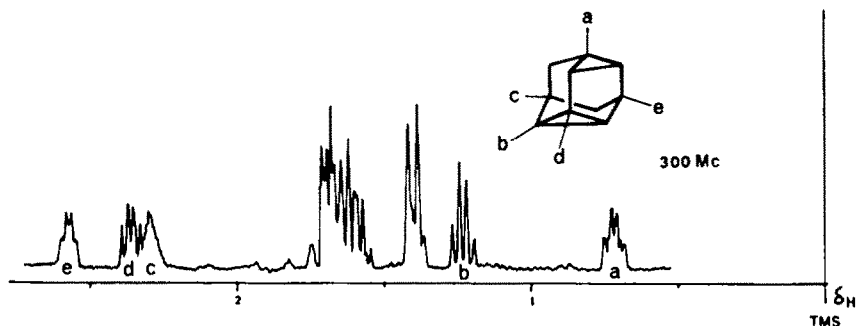
¶ Elemental micro analysis by H. Pieters, this laboratory, (Found: C, 90.38%; H, 8.94. $C_{10}H_{12}$ requires: C, 90.84; H, 9.15%).

TABLE 1. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 2-METHYLENEBICYCLO[3.3.1]NONA-3,6-DIENE (III) IN CCl_4 .

Proton	δ -value in ppm from internal TMS	Coupling constants in Hz
a,a'	1.82	$J_{a,d} = 3$; $J_{a,e} = 3$
b	1.96	$J_{b,c} = 18$; $J_{b,e} = 1.5$; $J_{b,h} = 4$
c	2.56	$J_{c,e} = 7$; $J_{c,h} = 3$
d	2.70	$J_{d,i} = 5.5$; $J_{d,j} = 5.5$
e	2.95	$J_{e,h} = 1$
f,g	4.83/4.88	
h	5.61	$J_{b,i} = 10$
i	5.95	
j,k	6.13	second order interactions.

From both IR and Raman spectra it was evident that one or probably two cyclopropane rings were involved in the molecule, as suggested by a strong band at 3035 cm^{-1} due to cyclopropane CH stretching vibrations.* Lack of absorption near 3060 cm^{-1} pointed to the absence of cyclopropane rings containing a CH_2 group.

The ^1H NMR spectrum at 100 MHz was rather obscure due to small differences between the chemical shifts of the protons and the occurrence of abundant spin couplings and second-order spin interactions. Spin decoupling experiments as well as

FIG. 2. ^1H NMR spectrum of IV in dioxane at 300 MHz.

* IRSCOT System (Infrared Structural Correlation Tables), Ed. R. G. J. Miller and H. Willes, Heyden and Son Ltd., London. L. J. Bellamy, *Advances in Infrared Group Frequencies*, Methuen and Co. Ltd., London, (1968).

measurements at 220 MHz* and 300 MHz† did not help identification of all separate proton signals. Only a few could be attributed to distinct protons using a model of the structure of the asymmetrical 2,4,6,9-tetrahydroadamantane (IV), as indicated in Fig. 2. The ^1H NMR spectra clearly showed isolated signals due to single protons (e.g. a and e in Fig. 2); the structures V and VI of isomeric pentacyclodecanes, represented in Fig. 3, could therefore be excluded since these exhibit elements of symmetry (m and 2C).

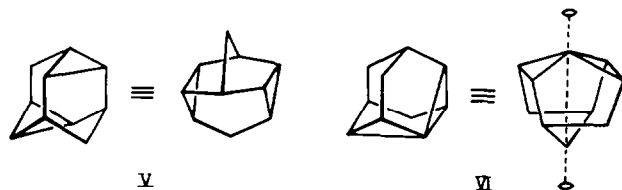


FIG. 3.

The only reasonable structure which thus remained was that of the pentacyclo[4.4.0.0^{2,10}.0^{3,5}.0^{4,8}]decane (IV) or trivially: 2,4,6,9-tetrahydroadamantane.‡ Eventually this structure could be confirmed by ^{13}C NMR spectroscopy.§ The spectrum (Fig. 4) showed ten different signals indicating ten different carbons. This presented unique proof of a molecule without any symmetry. Furthermore, by off-resonance techniques⁹ two of the signals could be recognized as originating from secondary carbons (CH_2) whereas the remaining eight signals were from tertiary carbons (CH). Since sufficient ^{13}C NMR data for strained hydrocarbons is not yet available, we are unable to attribute the observed signals unambiguously to distinct carbons. For comparison Fig. 4 contains the ^{13}C NMR spectrum of tetracyclo[4.3.1.0^{2,4}.0^{3,8}]decane (VII), trivially named 2,4-dehydroadamantane.^{2a}

Along with the structure determination by spectroscopy we tried to elucidate the structure of IV by chemical modification.^{2a, 10} The substance rapidly added bromine, but gave an intractable mixture of isomers. Addition of HCl also gave a complicated mixture of products. Catalytic hydrogenation^{2c} proved to be more successful and this presented chemical proof for the structure of IV.

When catalysed with Pt in THF with 1% AcOH, IV consumed one mole of hydrogen at room temperature and atmospheric pressure. Only two isomeric $\text{C}_{10}\text{H}_{14}$ hydrocarbons were obtained indicating the rather selective fission of one cyclopropane ring. The minor component (yield after isolation by GLC 10%) was identified as tetracyclo[4.3.1.0^{2,4}.0^{3,8}]decane (VII) by its IR spectrum.^{2a} The structure of the major

* 220 MHz NMR spectra recorded by P. E. J. Verwiël, Centraal Laboratorium, TNO, Delft, The Netherlands, on a Varian HR 220 Mc.

† 300 MHz NMR spectra recorded by Dr W. C. Jankowski, NMR applications Laboratories, Analytical Instrument Division of Varian, Palo Alto, California, USA.

‡ Name in accordance with Rule C-41 of the Definitive Rules for Section C of the Nomenclature of Organic Chemistry, I.U.P.A.C., 1965, Butterworths, London, 1965.

§ Proton noise decoupled ^{13}C NMR spectra were recorded on a Varian HA 100, equipped for ^{13}C resonance measurements, using multi scan averaging technique, by Dr W. C. Jankowski.

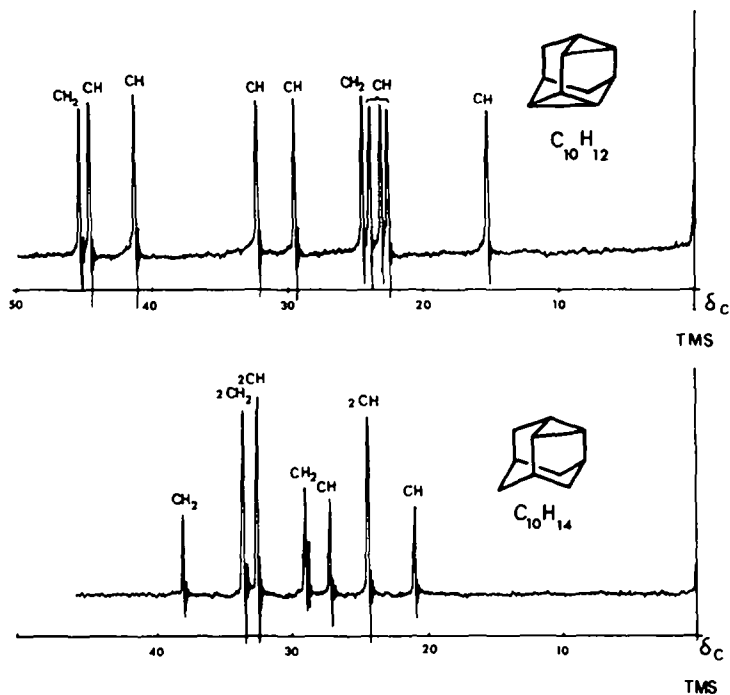


FIG. 4. ^{13}C NMR spectra of IV and VII in dioxane. (m.s.a., ^1H noise decoupled).

component (yield 60%) was established as tetracyclo[4.4.0.0².10⁴.8]decane (VIII) or trivial: 5,10-dehydroprotoadamantane, by the following reasoning. The isomers represented in Fig. 5 could, in principle, be expected on hydrogenolysis of one of the cyclopropane rings of IV:

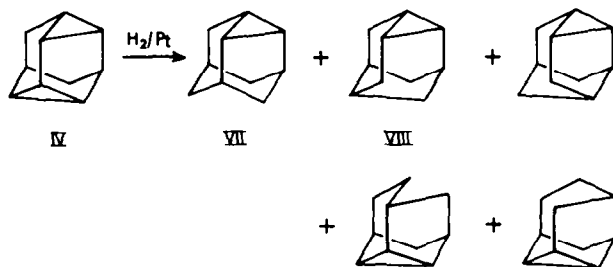


FIG. 5.

Of these isomers only VII and VIII exhibit a plane of symmetry. This property should lead to simplification in the ^1H NMR spectrum. Indeed, the ^1H NMR spectrum of the main product proved remarkably simple supporting a symmetrical structure. With the

model of VIII, redrawn in Fig. 6, the signals observed could be attributed to distinct hydrogens. The coupling constants were determined by spin decoupling and are collected in Table 2.

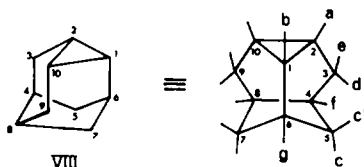


FIG. 6.

TABLE 2. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF TETRACYCLO[4.4.0.^{2,10}.0.^{4,8}]DECANE (VIII) IN CDCl₃.

Proton, cf. Fig. 6	δ -value in ppm from internal TMS	Coupling constants in Hz
a	0.74	$J_{a,b} = 8$; $J_{a,d} = 2$
b	1.06	$J_{b,g} = 8$
c,c'	1.29	$J_{c,g} = 1$
d	1.67	$J_{d,e} = 12$
e	1.96	
f	2.04	
g	2.57	

Another potential route for preparing a tetradehydroadamantane was by thermolysis of the di-lithium salt of 2,4-adamantanedione bis-tosylhydrazone (XI) instead of the 2,6-derivative. The 2,4-dione (X) was obtained conveniently by chromic acid oxidation of 4-hydroxy-2-adamantanone (IX).¹¹ Compound XI was prepared in a similar way to the 2,6-derivative (Fig. 7). Thermolysis of XI *in vacuo*, however, did not lead to an isolable quantity of the expected C₁₀H₁₂ hydrocarbon. The condensate obtained proved, by GLC analysis, to consist merely of a large number of products with low volatility. * Only a trace of a volatile component (< 0.5%) could be detected, it showed the same retention time as IV.

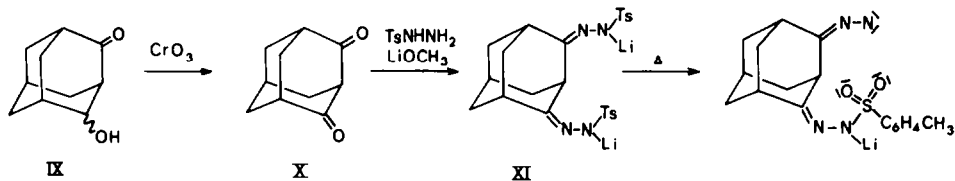


FIG. 7.

* Result independently obtained by J. H. Wieringa and H. Wynberg, University of Groningen, The Netherlands. We are indebted to Prof. H. Wynberg for this information.

Failure of formation of a volatile hydrocarbon from the 2,4-isomer must almost certainly be sought in the preference for insertion of the initially formed electron deficient nitrene or carbene into the adjacent tosylhydrazone group where many non-bonded electron pairs are available. This interaction is absent in the case of the 2,6-substituted product due to the greater distance between the two interfering sites of the molecule.

The question arises why IV is the only tetrahydroadamantane obtained after the thermolysis of II and why no symmetrical isomer like V is formed. Compound V, which is still unknown,¹² may be unstable and may have rearranged or polymerized immediately after its formation. The other possibility is that V has not been formed at all, which is conceivable in view of the following consideration. After the first cyclopropane ring has been formed, the energy barrier for insertion of the second-formed carbene (at C6) may be different with respect to the three potential sites of ring closure at C8, C9, or C10 (Fig. 8).

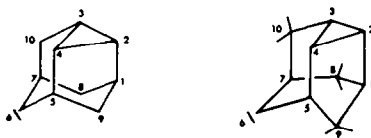


FIG. 8.

The ¹H NMR spectrum of 2,4-dehydroadamantane (measured at 300 MHz) showed different coupling constants of the protons at C9 with the vicinal protons at C1 and C5 (5 and 2 Hz, respectively). This indicates that the dihedral angles between the protons at C9 and those at C1 and C5 must be different and this points to a skeletal deformation in such a way that the five-membered ring, formed after the closure of the first cyclopropane ring, is flattened, resulting in a decrease of the distance between C6 and C9.

A molecular model,* although rather inadequate for these strained systems, suggests that C6 and C8, both being incorporated in a distorted cyclohexane ring, tend to move outwards. This will result in an increased C6–C8 interatomic distance rendering C8 less vulnerable for attack by the carbene located at C6.

Another aspect of this molecular deformation is that the orientation of the CH orbitals involved in the carbene insertion reaction at C8 or C9 are influenced in a different way. It seems probable that one of the C9 hydrogens moves into a more favourable position for migration to C6 (*cf.* the mechanism for transannular carbene insertion reactions^{5a}). Furthermore, by outward distortion of C6, its distance to C10 will be decreased and this also facilitates the transfer of the axial hydrogen from C10 to C6.† Carbene insertion into a CH bond of either C9 or C10 will result in the formation of the same asymmetrical tetrahydroadamantane. There is only a difference due to stereoisomerism.‡ Skeletal

* Of the available molecular model kits, the material of the "Prentice-Hall, Framework Molecular Models" solely allowed the construction of these strained systems.

† The interatomic distances could be estimated from the molecular model to be 2.4 Å for either C6–C9 or C6–C10 and 2.7 Å for C6–C8.

‡ In this preparation a racemate of the two optical antipodes would have been obtained in any event since the first cyclopropane ring can be formed either towards C4, C10, C8, or C9, which makes no difference with respect to the symmetry of the molecule.

deformation can thus be seen to render the route to the symmetrical tetradehydroadamantane (V) less attractive than to the asymmetrical isomer IV.

Valence isomerism transforms IV into its optical antipode (Fig. 9). Since the synthetic product is a non-resolvable racemate it is impossible to detect this isomerism polarimetrically. We therefore investigated the possibility of valence isomerism by variable temperature NMR. Spectra of IV were recorded in CFCl_3 at -67° and in CCl_4 at 80° and were identical apart from a slight line broadening at the low temperature. This, however, may be attributed to field inhomogeneity of the spectrometer and so there are no indications within this temperature range for thermally induced valence isomerism.



FIG. 9.

As to the structure of III it is clear that a rearrangement must have taken place after the thermolysis of II. We speculated whether III might be interconvertible with IV by isomerism as suggested in Fig. 10.*

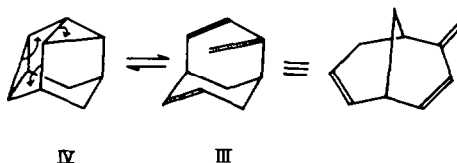


FIG. 10.

Thermal treatment of either III or IV at temperatures up to 200° , however, did not give any evidence of this interconversion. Both products may therefore originate from different precursors or from the same precursor but by different and thermally irreversible routes.

The thermal stability of IV under more severe conditions was tested at 400° for 10 min. A slightly yellow colour appeared and the m.p. was found to be lower. GLC analysis revealed, however, that no other volatile components had been formed. We therefore conclude that IV starts to decompose or to polymerize rather than to isomerize at this temperature.

The silver ion catalyzed isomerization of molecules with strained σ -bonds has been found to proceed smoothly in various instances.¹³ Compound IV was measured in benzene solution with and without AgBF_4 , but no difference in ^1H NMR spectra could be observed up to 80° , indicating that IV is stable under these circumstances.

* This isomerisation does not obey the definition of valence isomerism since a hydrogen shift must be involved.

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