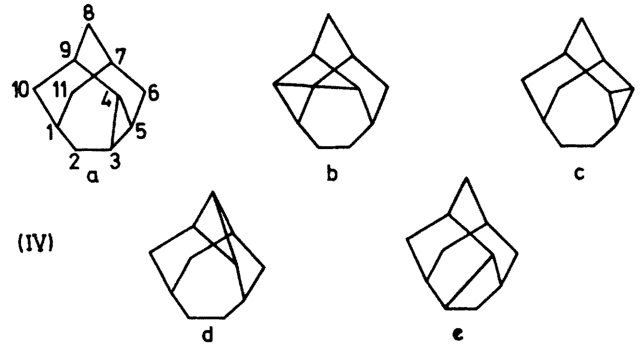
The Synthesis of 2,4-Dehydrohomoadamantane†

By ZDENKO MAJERSKI, SAMUEL H. LIGGERO, and PAUL VON R. SCHLEYER*
(*Department of Chemistry, Princeton University, New Jersey* 08540)

Summary 2,4-Dehydrohomoadamantane (IVa)† was prepared by the pyrolysis of the sodium salt of 4-homoadamantyl tosylhydrazone (I); hydrogenolysis of (IVa) gave homoadamantane exclusively.

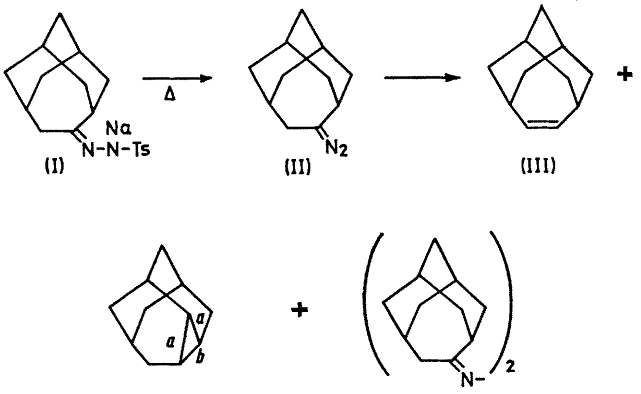
MANY strained polycyclic hydrocarbons have recently become available by the intramolecular insertion of appropriate carbenes.[1,2]

We report the simple preparation of 2,4-dehydrohomoadamantane (IVa)† (tetracyclo[$5,3,1,0^{3,5}0^{4,9}$]undecane) a novel hydrocarbon in the homoadamantane system. Unlike adamantane (T_d symmetry) which can give only one "non-bridgehead" dehydroadamantane[2a] homoadamantane (C_{2v} or C_2 symmetry)[3] can give rise to the five different "non-bridgehead" dehydrohomoadamantanes (IVa—e).‡



(IV)

Pyrolysis of 5·5 g of (I)[4,5] (obtained from 4-homoadamantanone[6] by the standard procedure[5]) was carried out at 170—180° (0·1 mm) for 1—2 h in a sublimator. As the reaction progressed, an orange-red solid which was shown to be 4-diazohomoadamantane (II) was collected on a cold



---

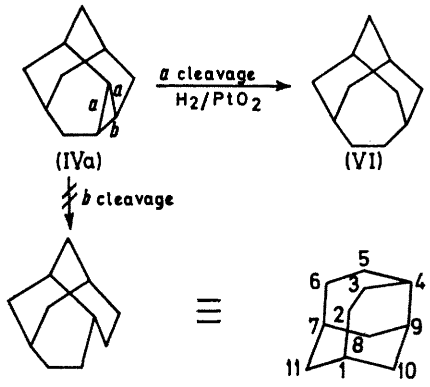
† Trivial nomenclature based on homoadamantane numbering.

‡ Two different types of dehydroadamantane and dehydrohomoadamantane can be considered: "non-bridgehead" (IVa—e) and "bridgehead" (bond formation between bridgehead positions). Only the former can, in principle, be obtained *via* carbene precursors.

finger. I.r. (CCl_4) $\nu(C{=}N_2)$ 2025s cm^{-1}; n.m.r. ($CDCl_3$) δ 1·2—2·8 (broad, complex multiplet). Upon standing at room temperature, (II) slowly decomposed to 1·4 g of a volatile white solid whose g.l.c. (Carbowax 20M, 175°) indicated the presence of two components (>98%) in the ratio 55 : 45. The compound of shorter retention time (55%) was shown by i.r., n.m.r., m.p., and comparison of retention time with an authentic sample to be 4-homoadamantene (III).[6] The other compound (m.p. 209—211°) gave a parent-ion signal (base peak) at *m/e* 148; i.r. (CCl_4), 3000m, 2900s, 2840m, and 1440m cm^{-1}; n.m.r. ($CDCl_3$) δ 0·6—2·3 (broad, complex multiplet). From these data and the method of synthesis the structure (IVa) was assigned§

To verify further the structure, (IVa) was hydrogenated in glacial acetic acid at 50° and 3 atm over PtO_2.[7] G.l.c. analysis (Carbowax 20M, 115°) of the resulting product indicated the presence of one compound which was shown to be homoadamantane (VI) by comparison with an authentic sample (i.r., n.m.r., g.l.c., m.p.). Evidently, either bond *a* cleaves in preference to bond *b*,[2f] since tricyclo[5,3,1,$0^{4,9}$]undecane (VII) was not detected in the hydrogenolysis product.

After removal of (II) further sublimation at 200° gave 0·5 g of a yellow solid (decomp. slowly >270°) whose m.s. (parent ion *m/e* 324, base peak 149), i.r. (CCl_4) $\nu(C{=}N)$ 1615s cm^{-1}, and n.m.r. ($CDCl_3$) δ 1·3—3·1 (broad multiplet) are consistent with the expected[5,6] structure (V), 4-homoadamantyl azine.‡



(IVa) (VI)

(VII) ≡ (VII)

This work was supported by grants from the National Institutes of Health and the Petroleum Research Fund Administered by the American Chemical Society. S.H.L. is an N.I.H. Postdoctoral Fellow, 1969—1970.

(*Received, May* 18*th*, 1970; *Com.* 770.)

---

§ Satisfactory analyses were obtained for all new compounds.

[1] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, 1959, **81**, 5512; W. R. Moore, H. R. Ward, and R. F. Merret, *ibid.*, 1961, **83**, 2019.

[2] (a) A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Comm.*, 1966, 657; (b) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, 1961, **83**, 3159; (*c*) P. K. Freeman, D. E. George, and V. N. Mallikarjuna Rao, *J. Org. Chem.*, 1964, **29**, 1682; (d) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, 1963, **46**, 1676; (e) M. H. Fisch and H. D. Pierce, jun., *Chem. Comm.*, 1970, 503; (*f*) P. K. Freeman, V. N. Mallikarjuna Rao, and G. E. Bigam, *ibid.*, 1965, 511.

[3] S. H. Liggero, P. von R. Schleyer, and K. C. Ramey, *Spectroscopy Letters*, 1969, **2**, 197.

[4] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, 1965, **87**, 935.

[5] M. Jones, jun., A. M. Harrison, and K. R. Rittig, *J. Amer. Chem. Soc.*, 1969, **91**, 7462.

[6] J. E. Nordlander, F. Wu, S. P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, 1969, **91**, 3962; P. von R. Schleyer, E. Funke and S. H. Liggero, *ibid.*, p. 3965; R. M. Black and G. B. Gill, *J. Chem. Soc.* (*C*), 1970, 671.

[7] C. W. Woodworth, V. Buss, and P. von R. Schleyer, *Chem. Comm.*, 1968, 569; Z. Majerski and P. von R. Schleyer, *Tetrahedron, Letters*, 1968, 6195, and references cited therein.