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A CONVENIENT, HIGH-YIELD PREPARATION OF DIAMANTANE (CONGRESSANE)

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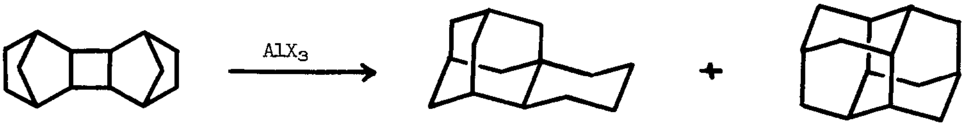
In 1965[1] the synthesis of Congressane (later renamed diamantane)[2] (I) was reported. Isomeric norbornene [2+2] dimers of general structure II[3] were used as starting materials. In the initial work with $AlCl_3$ as the catalyst, only about 1% yield of diamantane (I) resulted.[1,4] Since that time we have been attempting to improve the synthetic utility of such rearrangement routes. This objective has now been achieved with outstanding success. We summarize here the significant stages in this development, which now makes diamantane as readily available as adamantane.[5]

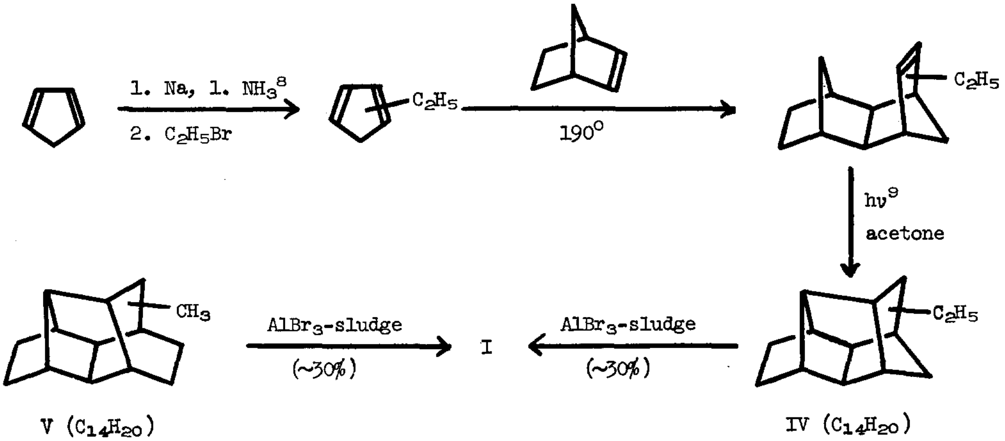


II ($C_{14}H_{20}$) III ($C_{14}H_{22}$) I ($C_{14}H_{20}$)

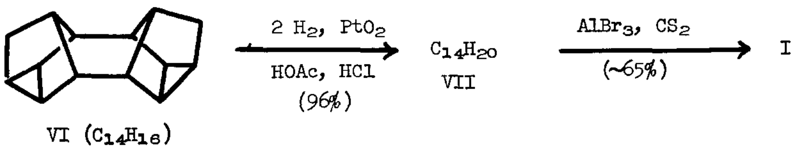
Three stereoisomers of structure II are known.[3] Of these, the least strained exo-trans-exo isomer, m.p. 63.5-64°,[3a] gives by far the best results; by use of an $AlBr_3$ "sludge" catalyst (prepared from $AlBr_3$ + t-butyl bromide),[6] 10-11% yields of diamantane (I) can be achieved.[2,6] The main product from any isomer of II, $C_{14}H_{20}$, is not diamantane (I), but is rather a tetracyclic disproportionation product, $C_{14}H_{22}$,[4] tentatively assigned structure III . The more highly strained isomers of II , such as the commonly available mainly endo-trans-exo material,[7] tend to give mostly disproportionation product (III) rather than diamantane (I) even with the $AlBr_3$-sludge catalyst.

To obtain better yields of diamantane (I), the use of of a less-strained starting material without labile cyclobutane rings was indicated. The fruitfulness of this approach was demonstrated by the observation that IV gave over 30% yield of diamantane with $AlBr_3$-sludge catalyst.

The disadvantage of this route lies in the relative unavailability of starting material (IV), the synthesis of which is outlined below. V, prepared similarly, gives comparable yields of diamantane (I).



Various non[2+2]dimers of norbornadiene are known.[10-12] The most readily available of these, "Binor-S" (heptacyclo$[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]$tetradecane)[11c] (VI),[11] easily prepared by using $CoBr_2(\phi_3P)_2$ + $BF_3.OEt_2$ catalyst,[11b] proves to be ideal for the preparation of diamantane (I). Hydrogenation of VI in glacial acetic acid solution with added hydrochloric acid at 80° under 3 atmospheres hydrogen pressure[12] gave a tetrahydro product (VII, an oil, b.p. 105-110° at 1.5mm) nearly quantitatively. This hydrogenated material (VII), mainly a single isomer of yet undetermined structure, isomerizes to diamantane in an average yield of 65%! The rearrangement conditions are very simple: VII is dropped slowly into a carbon disulfide or cyclohexane solution of good quality $AlBr_3$ (one quarter of the weight of VII). The reaction is gently exothermic. After the addition is complete, and refluxing subsides, the mixture is heated with stirring for an additional 1/2-1 hour. The reaction course can be monitored by glpc. Occasionally the addition of more $AlBr_3$ is needed to complete the reaction. Recrystallization of the product from pentane gives m.p. 244.0-245.4° (reported m.p. 236-237°).[1]



Because of its larger size and lower symmetry, diamantane may have even greater potential than adamantane[5] for synthetic, pharmacological and mechanistic purposes. We have already worked out methods for the introduction of substituents into the three different positions on the carbon skeleton.[6,14] Methyl and polyalkyldiamantanes can also be prepared by rearrangement. Details of the chemistry of diamantane will be described subsequently.

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(3) (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, ibid., **87**, 2596 (1965).
(b) E. B. Whipple and M. Ruta, ibid., **87**, 3060 (1965).
(c) G. N. Schrauzer, Adv. Catalysis, **18**, 373 (1968).

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(6) V. Z. Williams, Jr., A. B. Thesis, Princeton University, 1965. Confirmed by Dr. C. Hoogzand, ERA Laboratory, Brussels, private communication.

(7) Endo-trans-exo-II is the major isomer in the product obtained by acetone phosensitized dimerization of norbornene (D. Scharf and F. Korte, Tetrahedron Lett., 821 (1963) The stereochemical assignments were later revised.[3] This mixture was used by Landa to obtain ~1% yield of diamantane.[4] Commercially available [2+2] norbornadiene dimer (Aldrich) also consists mostly of the endo-trans-exo isomer, and its hydrogenation product is not a very satisfactory starting material for the preparation of diamantane (I).

(8) K. Alder and H. J. Ache, *Ber.*, **95**, 503 (1962).

(9) *Cf.* H.-D. Scharf, *Tetrahedron*, **23**, 3057 (1967).

(10) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966). In our hands, yields of this dimer have been erratic. Furthermore, while the dihydro derivative, $C_{14}H_{18}$, is easily prepared by catalytic hydrogenation, hydrogenolysis of the three-membered ring (to give a $C_{14}H_{20}$ isomer of I) is surprisingly difficult. Were it not for these problems, the Katz dimer would be a reasonably good starting material for diamantane preparation.

(11) (a) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *ibid.*, **88**, 4890 (1966).
(b) G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *Tetrahedron Lett.*, 543 (1970).
(c) The originally proposed[11a] von Baeyer IUPAC name for "Binor-S" is incorrect.

(12) H.-D. Scharf, G. Weisgerber, and H. Höver, *Tetrahedron Lett.*, 4227 (1967) and literature therein cited.

(13) *Cf.* C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968); Z. Majerski and P. v. R. Schleyer, *Tetrahedron Lett.*, 6195 (1968).

(14) See R. C. Fort, Jr., and P. v. R. Schleyer, *Advances in Alicyclic Chemistry*, **1**, 283 (1966).