Tetrahedron Letters No.4, pp. 415-418, 1966. Pergamon Press Ltd.
Printed in Great Britain.

SYNTHESIS OF HEXAOXADIAMANTANES

O. Vogl and B. C. Anderson

Central Research Department*

D. M. Simons

Elastomer Chemicals Department

E. I. du Pont de Nemours and Company,
Experimental Station, Wilmington, Delaware

(Received 16 November 1965)

Adamantane (I) has been known for many years. Prelog[1] has called the synthesis of the next higher member (I) of the series a challenge for an organic chemist. The structure of this compound was used as the emblem for the XIX IUPAC Congress in London, July, 1963; and the compound itself was called by Prelog[1] "congressane" (II). An elegant synthesis of this compound has recently been reported by Schleyer.[2]

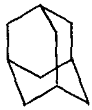
A congressane-type structure was proposed by Weissbach[3] for scyllitol diborate; it was based on elemental analysis only. We have reason to believe that this compound is actually a polymer. We were interested in the synthesis of heteroatom analogs of II and wish to report the synthesis of compounds III and IV.

---

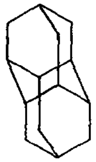
* Contribution No. 1067 from the Central Research Department.

We propose to use the name "diamantane"[*] for structure II.[***]

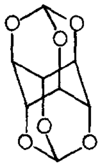
Compound III is referred to in this paper as hexaoxadiamantane and IV as diphosphahexaoxadiamantane.



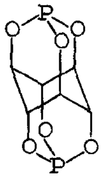
I



II



III



IV

---

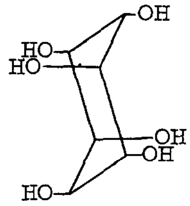
[*] While the name "congressane" has historic value, the name "diamantane,"[**] implying that it is the second member of an adamantalogous series, whose three-dimensional ultimate is diamond, appears to have more general usefulness. Triamantane and tetramantane would then be the logical names for the next "linear" members of the adamantalogous series.

Although the name diamantane was once very briefly used for structure I, adamantane [O. Böttger, Ber. deut. chem. Ges. 70B, 314 (1937)], it has long been abandoned. Hence, reintroduction of the term for the second member of the series should cause no confusion.

[**] We have been in correspondence with P. von R. Schleyer in connection with this nomenclature of adamantalogous series, and we have reached agreement on the use of the name diamantane for congressane.

[***] Based upon the Geneva rules of nomenclature, the name of II is pentacyclo$[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]$tetradecane, the name for hexaoxadiamantane III is 3,5,8,10,13,14-hexaoxapentacyclo-$[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]$tetradecane, and for structure IV: 4,9-diphospha-3,5,8,10,13,14-hexaoxapentacyclo$[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]$-tetradecane.

Hexaoxadiamantane (III) was prepared in 15% yield by reaction of scyllitol with excess triethyl orthoformate in dimethyl sulfoxide (DMSO) at 200°*. The excess orthoformate and DMSO were removed under reduced pressure, and the residue was sublimed. The sublimate was purified by recrystallization from dioxane and resublimation (80°/0.1 mm.). The hexaoxadiamantane melted at 303-305° (sealed tube).



$+ \ 2HC(OC_2H_5)_3 \longrightarrow \text{III} + 6C_2H_5OH$

Anal. Calcd. for $C_8H_8O_6$: C, 48.01; H, 4.03; O, 47.96. Found: C, 48.34; H, 4.22; direct O, 47.11.

The compound showed no indications of decomposition when heated to 400° in a sealed tube; it was, however, hydrolyzed to scyllitol with 6N HCl. The infrared spectrum showed no hydroxyl or carbonyl absorption. The NMR spectrum in deuterochloroform showed two kinds of protons in a 3:1 ratio at -4.71 and -5.67 ppm., respectively (tetramethylsilane standard). Mass spectroscopic analysis gave a high intensity peak occurring at 200, the molecular weight of hexaoxadiamantane.

---

* The method used by H. Stetter and K. H. Steinacker, Ber. deut. chem. Ges. 86, 790 (1953), for preparation of trioxaadamantanes from cis-phloroglucitol is not operable with scyllitol.

In a similar manner, diphosphahexaoxadiamantane was prepared by reaction of scyllitol with trimethyl phosphite. The product sublimed at 110°/0.2 mm. and melted at 276-280° (sealed tube).

Anal. Calcd. for $C_6H_6O_6P_2$: C, 30.52; H, 2.56; P, 26.26; mol. wt., 236.06. Found: C, 30.46; H, 2.78; P, 26.09, 26.53.

The mass spectrum showed that the compound had little tendency to fragment. The most abundant ion was mass 236. The isotopic abundancies agreed well with theory; for example, mass 237 was calculated to be 6.7%, found 6.9%. The proton NMR spectrum showed a single resonance at -4.75 ppm. from tetramethyl silane. At high resolution this resonance showed complex splitting, perhaps due to interaction with the phosphorus atoms.

REFERENCES

1. V. Prelog, Pure Appl. Chem. 6, 545 (1963); G. M. Blackburn, D. L. Cameron, A. R. Katritzky, and R. H. Prince, Chem. and Ind. (London) 1349 (1963).
2. C. Cupas, P. von R. Schleyer, and D. J. Trecker, J. Amer. Chem. Soc. 87, 917 (1965).
3. A. Weissbach, J. Org. Chem. 23, 327 (1958).