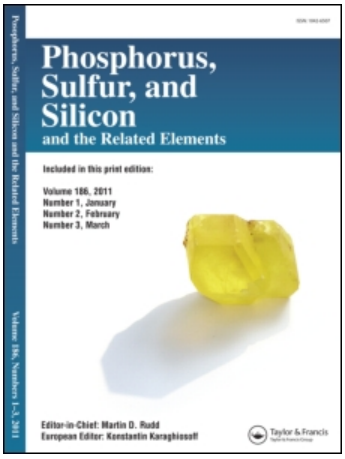


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Phosphaadamantane

Hendrik J. Meeuwissen[a]; Theodorus A. Van Der Knaap[a]; Friedrich Bickelhaupt[a]
[a] Vakgroep Organische Chemie, Vrije Universiteit, HV Amsterdam, The Netherlands

To cite this Article Meeuwissen, Hendrik J. , Van Der Knaap, Theodorus A. and Bickelhaupt, Friedrich(1983) 'Synthesis of Phosphaadamantane', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 109 — 112
To link to this Article: DOI: 10.1080/03086648308075979
URL: http://dx.doi.org/10.1080/03086648308075979

Phosphorus and Sulfur, 1983, Vol. 18 pp. 109-112
0308-664X/83/1801-0109/$18.50/0

SYNTHESIS OF PHOSPHAADAMANTANE

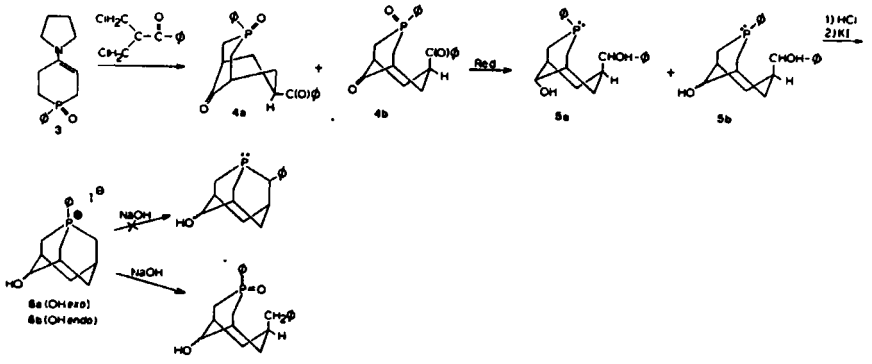
HENDRIK J. MEEUWISSEN, THEODORUS A. VAN DER KNAAP,
FRIEDRICH BICKELHAUPT
Vakgroep Organische Chemie, Vrije Universiteit,
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract Phosphaadamantane (1), a cage compound with a phosphorus atom on a bridgehead position, is of interest in organoelement chemistry. We wish to report the synthesis of 1 and 2[1] a derivative of 1, which are the first examples of phosphaadamantanes without additional heteroatoms in the skeleton.

SYNTHESIS

Our synthetic approach of 1 and 2 was inspired by the strategy developed by Speckamp ea.[2a,b] for azaadamantane (Scheme 1).

Scheme 1

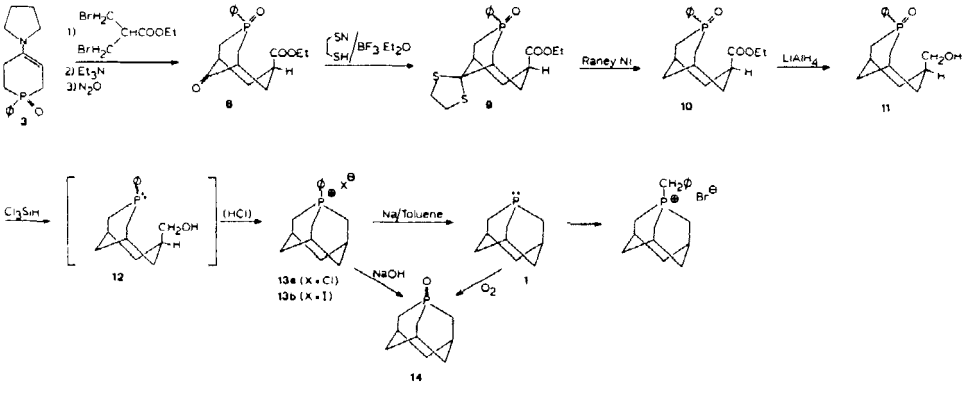


Key step in both synthesis is an α,α'-annelation of a 1,3-dihalide with the enamine of the phosphorinanone oxide 3. In the synthesis of 2, the dihalide was 1,3-dichloro-2-benzoylpropane. Two bicyclic phosphine oxides 4 were formed, which could be separated by crystallization. The structure of these isomers was confirmed by X-ray structure determination. Structural differences consisted main-

ly in the *exo*- and *endo*-position of the phosphorus-bound phenyl-ring and the chair or boat form of the basal cyclohexane ring. Both isomers could be reduced to the phosphines 5 and ring closure under acid catalysis gave the phosphoniaadamantanes 6. From 5a, pure 6a was obtained; from 5b, which was a mixture of the *exo*- and *endo*-7-hydroxy-isomers 6a and 6b were formed. Unfortunately, the yields were low (5.5% from 5a and 11% from 5b). Remarkable is the ring closure of 5b, because the lone pair points in the direction opposite to that required for attack on the ring closing carbon atom. Acid catalysed inversion of configuration at phosphorus is considered to account for this ring closure. The structure of the *exo*-isomer 6a was confirmed by X-ray structure determination. Unfortunately, our final goal, the tertiary phosphine derived from 6a, could not be reached as the conversion of 6 to a phosphaadamantane oxide by NaOH failed; the phenyl phosphorus bond was not cleaved, but ring opening occurred instead, which is favoured because of the benzylic nature of the P-C(2) bond.

The synthetic approach to the phosphaadamantane skeleton had thus proven to be successful, even though the yields were not high. Therefore we repeated the reaction sequence starting with the 1,3-dibromide 7 containing an ester group instead of the phenyl ring, which has caused so much trouble in the final stage. (Scheme 2).

Scheme 2



The α,α-annelation yielded 59% of the bicyclic oxides 8. ^{31}P NMR spectra revealed that only 2 of the 16 possible isomers were formed. From earlier work on the nitrogen analogues and the structure of the oxides 3 it is highly probable that the ester group occupies the *endo*-position. Consequently the two isomers must differ in the configuration at phosphorus.

The removal of the keto function in 8 by conversion of the dithioketal 9, followed by reduction with Raney-nickel to 10, was achieved in 59% overall yield. The reduction of 10 to 11 with lithium aluminum hydride occurred almost quantitatively. The intermediate products 9, 10 and 11 were characterized by their NMR and mass spectra and used without further purification. In analogy to the synthesis of 2, we next envisaged the reduction of 11 with trichlorosilane to 12 which than would be cyclized to 13a by the action of methanolic HCl. However, when actually performing the reaction, it appeared that the second step occurred spontaneously, probably under the influence of traces of HCl which might be formed as a byproduct in the reduction. After addition to potassium iodide and crystallization from ethanol/water, 13b was isolated in 34% yield; this yield is much higher than that leading to 2[1]. The elemental analysis and the field desorption mass spectrum of 13b (m/z = 231, rel. intensity 100%, 13^+. the phosphonium ion part of 13b) were in agreement with the assigned structure, as was the ^1H NMR spectrum; characteristic is the ^{13}C NMR spectrum which - in contrast to those of all precursors - reflects the C_{3v} symmetry of the skeleton of 13b by its very simple appearance, i.e. 3 signal in the aliphatic region; the solvent-dependant ^{31}P NMR signals was found at δ=4.8 ppm ($CDCl_3/CF_3COOD$) or δ=9.1 ppm (CD_3OD/D_2O).

As expected, and in contrast to 2, the removal of the phenyl substituent from 13b posed no problems. Boiling 13b with NaOH in ethanol/water gave the tertiary phosphine oxide 14 in quantitative yield; the spectral data were in full agreement with the assigned structure δ(^{31}P)=34.8 ppm.

Treatment with sodium in refluxing toluene gave 1 in 64% yield as a white solid. Again, the NMR spectra are very simple: three broad signals in the ^{1}H NMR spectrum (δ=1.87, 1.89, 1.95 ppm, assignment not yet possible), three signals in the ^{13}C NMR spectrum (δ=21.2 {CH}, 22.5 {P-CH_2}, 31.8 ppm {CH-CH_2-CH}), with the expected proton and phosphorus couplings. The phosphorus chemical shift of 1 (δ=-59.0 ppm) is unexpectedly low as compared to that of its close structural analogue 1,3,5-triaza-7-phosphaadamantane[3] (δ=-101.6 ppm). However, it compares favourably with chemical shift values for normal tertiary phosphines; an empirical approach based on increments predicts δ=-45.5 ppm. The slight upfield shift for 1 compared to the predicted value may, with appropriate caution, be taken as evidence for very slight residual strain in the molecule.

1 could be converted to phosphoniaadamantane with benzyl bromide in benzene at room temperature (yield 24%). With oxygen 1 was oxidized to 14. Other aspects of the chemistry of 1 are presently being investigated. The results will be presented together with a more detailed analysis of spectral and structural properties of 1.

REFERENCES

1. H.J. Meeuwissen, G. Sirks, F. Bickelhaupt, C.H. Stam, A.L. Spek, Rec. Trav. Chim. Pays-Bas 101, 443 (1982).
2. a. W.N. Speckamp, J. Dijkink, H.O. Huisman, J. Chem. Soc. Chem. Commun. 197, (1970); b. Th. Reints Bok, W.N. Speckamp, Tetrahedron 35, 267 (1979).
3. E. Fluck, J.E. Förster, Chemiker Z. 99, 246 (1975), K.H. Jogun, J.J. Stonowski, E. Fluck, H.J. Weissgraeter, Z. Naturforsch. 336, 1257 (1978).