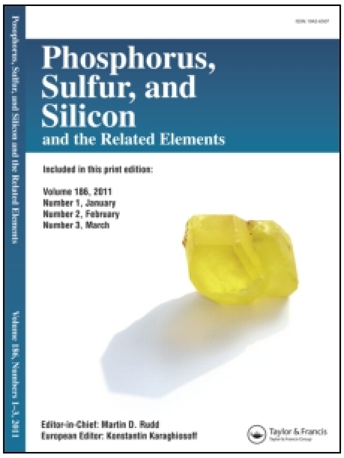


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Mediated Cyclooligomerization of Phosphaalkynes-New Aspects in the Synthesis of Polycyclic Phosphorus Compounds [1]

Manfred Regitz[a]; Thomas Wettling[a]; Bernhard Breit[a]; Manfred Birkel[a]; Bernhard Geissler[a]; Uwe Bergstrasser[a]; Stefan Barth[a]; Paul Binger[a]
[a] Department of Chemistry, University of Kaiserslautern, Kaiserslautern, FRG

To cite this Article Regitz, Manfred , Wettling, Thomas , Breit, Bernhard , Birkel, Manfred , Geissler, Bernhard , Bergstrasser, Uwe , Barth, Stefan and Binger, Paul(1993) 'The Mediated Cyclooligomerization of Phosphaalkynes-New Aspects in the Synthesis of Polycyclic Phosphorus Compounds [1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 1 — 4

To link to this Article: DOI: 10.1080/10426509308032343

URL: http://dx.doi.org/10.1080/10426509308032343

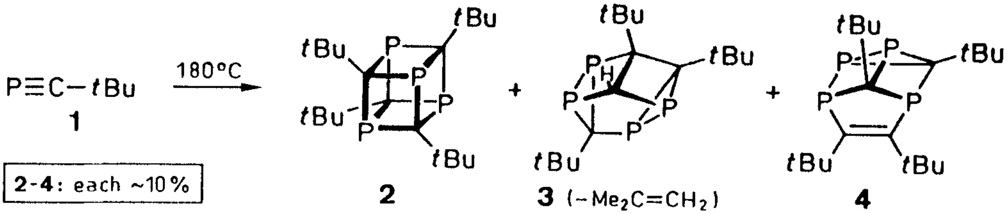
Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 1–4
Reprints available directly from the publisher
Photocopying permitted by license only

THE MEDIATED CYCLOOLIGOMERIZATION OF PHOSPHAALKYNES - NEW ASPECTS IN THE SYNTHESIS OF POLYCYCLIC PHOSPHORUS COMPOUNDS [1]

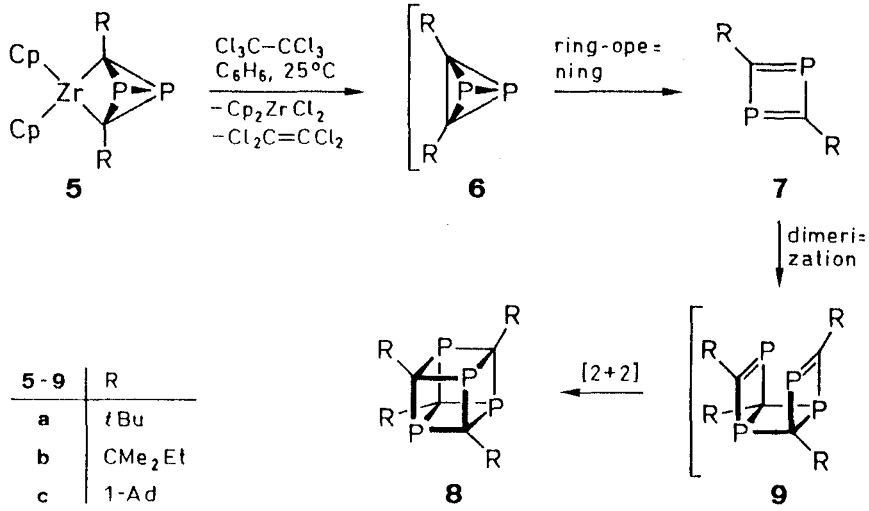
MANFRED REGITZ, THOMAS WETTLING, BERNHARD BREIT, MANFRED BIRKEL, BERNHARD GEISSLER, UWE BERGSTRÄSSER, STEFAN BARTH, PAUL BINGER
Department of Chemistry, University of Kaiserslautern,
Erwin-Schrödinger-Straße, D-6750 Kaiserslautern, FRG

Abstract Cyclooligomerization reactions of phosphaalkynes make a great variety of polycyclic phosphorus compounds (**2-4**, **10-15**, **20**, **21**) readily available.

The uncatalyzed thermal cyclooligomerization of phosphaalkyne **1** [2] leads first of all to the formation of cyclotetramers having cubane (**2**), cuneane (**3**) and bis(homo)prismane structure (**4**) [3].

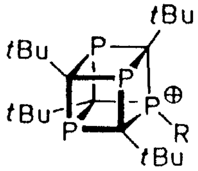


Cubane formation is optimal [⟶ **8a-c**(**8a**≡**2**)] and barely accompanied by side-products when the zirconium complexes **5** [4] are treated with hexachloroethane [5]. We presume that the diphosphatetrahedrane **6**, the diphosphete **7** as well as the tricyclic bis(phosphaalkene) **9** are intermediates in the formation of the pentacyclic compounds. Evidence for the intermediacy of **7** comes from the isolation of its $Fe(CO)_3$-complex which is formed when the $Fe(CO)_4$-complex of **5** is treated with hexachloroethane [5].

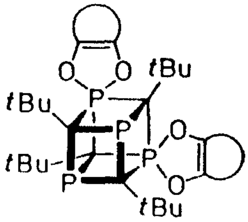


5-9	R
a	*t*Bu
b	CMe$_2$Et
c	1-Ad

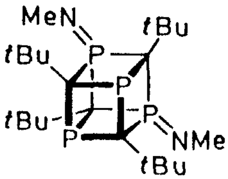
Tetraphosphacubane **8a** (≡**2**) - now available in high yields - can be functionalized at the phosphorus atoms though their nucleophilicity has been reduced dramatacally by participation of the P-"lone-pair" in the σ-P-C-bonding. Alkylation with methyl triflate as well as complex formation with nonacarbonyl diiron only takes place at one phosphorus atom [→ **10a**: R=CH$_3$, CF$_3$SO$_3$$^-$; **10b**: R=Fe(CO)$_4$$^-$] even with an excess of the reagents.



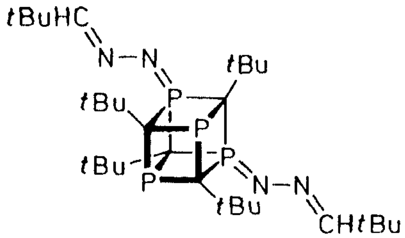
10



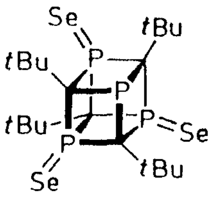
11



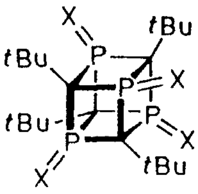
12



13



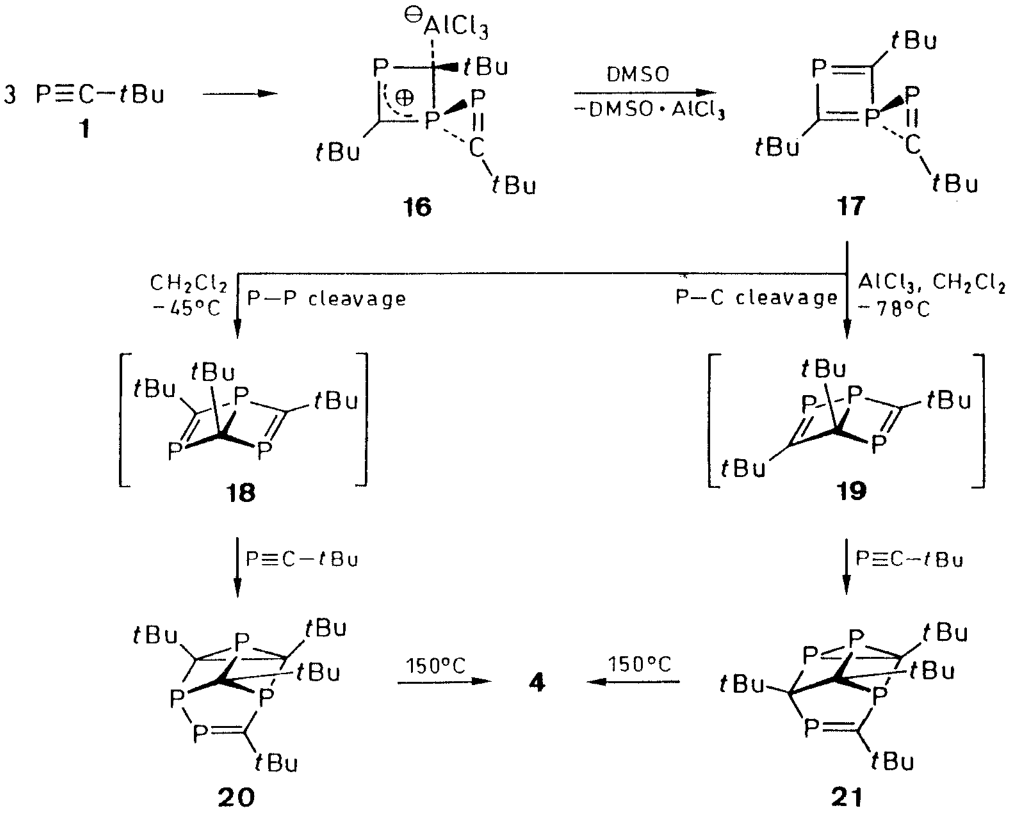
14



15

A twofold [4+1] cycloaddition is observed with two equivalents of tetrahalogeno ortho quinones to yield the spirocyclic compounds of type **11**[6].The same degree of substitution is observed in the Staudinger-reaction with methyl azide (→ **12**) and in the phosphazine formation with diazo compounds (→ **13**)[6]. In the selenation reaction three phosphorus atoms are attacked (→ **14**), whereas the oxidation with elemental sulfur or bis(trimethylsilyl)peroxide results in a complete transformation of the $\lambda^3\sigma^3$- into $\lambda^5\sigma^4$-phosphorus atoms (**15**, X=S,O)[6].

The Lewis-acid induced cyclooligomerization of phosphaalkynes opens a new field in the chemistry of low-coordinated phosphorus. If the phosphaalkyne **1** and aluminium chloride are reacted in a ratio of 3:1, the spirocyclic betaine **16** can be isolated in excellent yield (> 90%)[7]. Removal of the Lewis acid, e.g. with dimethylsulfoxide generates the 1,3-diphosphete **17** having both a $\lambda^3\sigma^2$- and a $\lambda^5\sigma^4$-phosphorus atom.



This high-energy compound rearranges under the formation of Dewar-triphosphabenzenes (**18** by P-P cleavage, **19** by P-C cleavage under assistance of an excess of $AlCl_3$), which can be trapped by homo-Diels-Alder-reaction with **1** as cycloaddition partner to form the tetracyclic tetraphosphaoctenes **20** and **21**. Compounds of this type represent isomers of **8a**(≡**2**) and can be transformed by thermal means into **4**[7].

A detailed discussion of the rection mechanisms as well as convincing arguments for the structure of the isolated compounds have been given in the oral presentation of this work.

ACKNOWLEDGMENT

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support. B. Breit is grateful to the Fonds der Chemischen Industrie while M. Birkel and B. Geißler are indebted to the Landesregierung von Rheinland Pfalz for post graduate grants.

REFERENCES

[1] Organophosphorus Compounds; Part 62. For Part 61, see: M. Regitz, P. Binger, M. Birkel, B. Breit, S. Haber, J. Hoffmann, H. Memmesheimer, O. Wagner, T. Wettling and H. Heydt, Bull. Soc. Chim. Belg., 101, 359 (1992).

[2] Reviews: M. Regitz and P. Binger, Angew. Chem., 100, 1541 (1988); Angew. Chem. Int. Ed. Engl., 27, 1485 (1988); M. Regitz, Chem. Rev., 90, 191 (1990); M. Regitz and P. Binger in Multiple Bonds and Low Coordination in Phosphorus Chemistry, edited by M. Regitz and O. J. Scherer (Thieme, Stuttgart 1990), Chap.C2, pp.58-111.

[3] T. Wettling, J. Schneider, O. Wagner, C. Kreiter and M. Regitz, Angew. Chem., 101, 1035 (1989); Angew. Chem. Int. Ed. Engl., 28, 1013 (1989).

[4] P. Binger, B. Biedenbach, C. Krüger and M. Regitz, Angew. Chem., 99, 798 (1987); Angew. Chem. Int. Ed. Engl., 26, 764 (1987).

[5] T. Wettling, B. Geißler, R. Schneider, S. Barth, P. Binger and M. Regitz, Angew. Chem., 104 (1992),in press; Angew. Chem. Int. Ed. Engl., 31 (1992), in press.

[6] M. Birkel, U. Bergsträßer, J. Schulz and M. Regitz, Angew. Chem., 104 (1992), in press; Angew. Chem. Int. Ed. Engl., 31 (1992), in press.

[7] B. Breit, U. Bergsträßer, G. Maas and M. Regitz, Angew. Chem., 104 (1992), in press; Angew. Chem. Int. Ed. Engl., 31 (1992), in press.