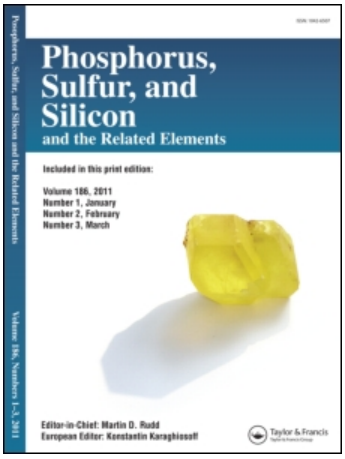


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Preparation and Structure Investigation of 2,3-Dihydro-1,3-Benzothiazole-3,2-d-1,2,4, 3-Triazaphosphole

Jinglin Zhang[a]; Zhisong Cao[a]
[a] Inst. of Org.Synth., Huazhong Normal University, Hubei, People's Republic of China

To cite this Article Zhang, Jinglin and Cao, Zhisong(1987) 'Preparation and Structure Investigation of 2,3-Dihydro-1,3-Benzothiazole-3,2-d-1,2,4, 3-Triazaphosphole', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 531 — 534
To link to this Article: DOI: 10.1080/03086648708080637
URL: http://dx.doi.org/10.1080/03086648708080637

Phosphorus and Sulfur, 1987, Vol. 30, pp. 531–534
Photocopying permitted by license only

PREPARATION AND STRUCTURE INVESTIGATION OF 2,3-DIHYDRO-1,3-BENZOTHIAZOLE-3,2-d-1,2,4,3-TRIAZAPHOSPHOLE

JINGLIN ZHANG, ZHISONG CAO
Inst. of Org.Synth., Huazhong Normal University,
Wuhan, Hubei, People's Republic of China

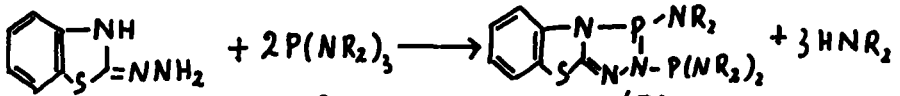
Abstract The first represantatives of derivatives of title compound were synthesized and their interested structure was investigated.

INTRODUCTION

Fused tricyclic triazaphosphole have so far not been described, except for the dimers of a few monocyclic triazaphosphole with pentacoordinated phosphorus[1,2]. We reported here the first represantatives of derivatives of the title compound.

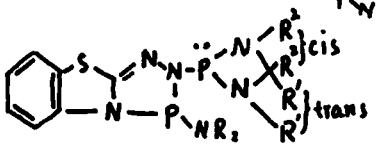
3-DIALKYLAMINO-2-BIS(DIALKYLAMINO)PHOSPHINO- DERIVATIVES

The intermolecular cyclocondensation of A[3] with B affords (I)[4].



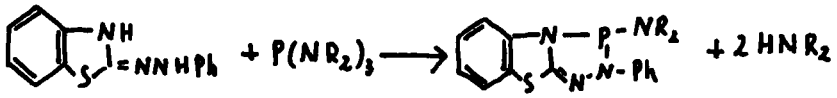
A B (I)

They are very sensitive to moisture and decompose under acidic condition. It was found that the stronger electrondonor the R group, the larger the $^{2}J(PNP)$ value in their ^{31}P NMR spectra.

According to the IR and ^{1}H and ^{13}C NMR spectra the plane  is perpendicular to suggested planar ring system, R^2 stands at cis and R^1 at trans to the lone pair of phosphorus atom[5].

3-DIALKYLAMINO-2-PHENYL DERIVATIVES

Compound C[3] reacts with B to afford (II)[4] which give fused tricyclic ring cation as the base peak in MS spectra.



C B (II)

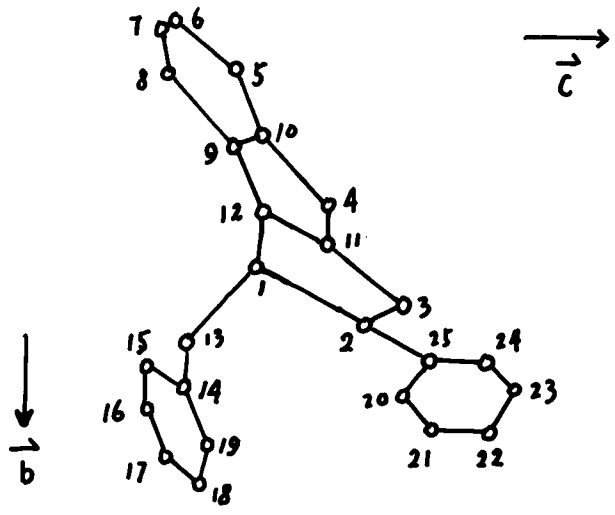
In ^{13}C NMR spectra a long range ^{4}J and a strong ^{3}J were observed only between P and aromatic C.

3-AROXY(or THIOARYL)-2-PHENYL DERIVATIVES

The reaction of (II)(R=Et) with D gives (III)[6]. It was

(II) D (III) X=O or S

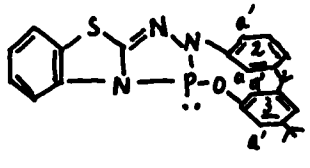
noted that an electrondonating substituent on Ar moves chemical shift of P to higher field and an electronwithdrawing to the lower. The crystalline structure of (III, Ar=Ph) was determined by X-ray diffraction. It is monoclinic geometry. The sums of bond angles around the atoms connecting two rings, as C(9),C(10),C(11) and N(12), equal to about 360°. The bond lengthes in the ring are shorter than usual single bonds. So this fused ring system has a planar structure. The PhO group is located at endo to the ring system rather than the exo position.



Bond Angles

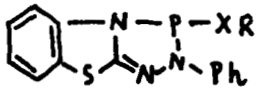
N(12)-C(11)-S(4)	111.7°	C(11)-N(12)-C(9)	114.7°
N(3)-C(11)-S(4)	129.9°	C(9)-N(12)-P(1)	133.6°
N(12)-C(11)-N(3)	118.4°	C(11)-N(12)-P(1)	111.7°
C(9)-C(10)-S(4)	111.5°	C(10)-C(9)-N(12)	112.3°
C(5)-C(10)-S(4)	127.5°	C(10)-C(9)-C(8)	121.3°
C(5)-C(10)-C(9)	111.7°		

The ^{13}C and ^{1}H NMR spectra showed that if (III) contains an o- or m-substituted phenoxy group, as in the case of (III,Ar=3,5-$Me_2C_6H_3$), the Ph and $Me_2C_6H_3O$ groups stand parallelly to each other and perpandicularly to the fused ring at all. C_{2a} situated nearer to the lone pair of phosphorus than $C_{2a'}$. This is ture too for C_a and $C_{a'}$ in ring 3.

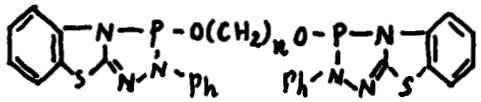


3-ALKOXY(or THIOALKYL)-2-PHENYL DERIVATIVES

Compounds (IV) and(V) can be obtained from the reaction of (II,R=Et) with various alcohols, thiols and diols respectively. ^{1}H NMR showed that if R group in(IV) has a straight chain, only O-C bond cannot rotate along its

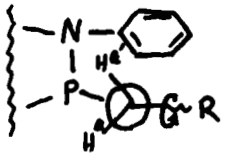


(IV) (X=O or S)

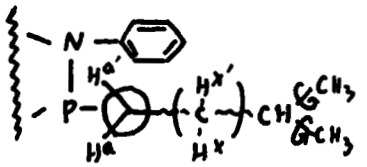


(V) (n ≥ 2)

axis, all the other C-C bonds are free; if R group is a branching one, then only the terminal two C-C bonds in $CH(CH_3)_2$ group can freely rotate along their axes, the rotation of the other C-C bonds is restricted.



(IV) with straight chain R



(IV) with a branching chain R

THE AMINO-EXCHANGING REACTION OF (II)

The amino-exchanging reaction of (II) readily occurs with secondary aliphatic amines but rather difficultly with primary aliphatic amines. The products obtained from (II) and aromatic amines are not stable due to the presence of steric hindrance.

REFERENCES

1.Schmidpeter,A.,Tautz,H.,Z.Naturforsch 6 35,1222(1980)
2.Schmidpeter,A.,Luber,J.,Tautz,H.,Angew.Chem.89,554(1977);Angew.Chem.,Intd.Engl.,16,546(1977)
3.Cao,Z.S.,Zhang.J.L.,Centr. China Teach. Coll. Natur. Scin. Ed.,3,69(1984)
4.Zhang,J.l.,Cao Z.S.,Synthesis,(11),1067(1985)
5.Zhang,J.L.,Cao,Z.S.,Kexue Tongbao,(6),432(1986)
6.Zhang,J.L.Cao,Z.S., Huaxue Xuebao,44,(1),51(1986)
7.Cao,Z.S.,Zhang,J.L.,Xu,K.F.,Chin.J.Microw.Radio-Freq. Spect.,3,(2),99(1986)