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1,4,2-Diazaphospholidine-3,5-diones and Related Compounds: A Lecture on Unpredictability in Catalysis

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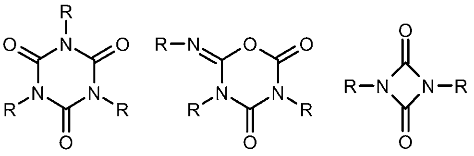
This article is dedicated to Prof. Dietmar Seyferth on the occasion of his 80th birthday.

Trivalent phosphorus compounds have long been used as catalysts in isocyanate chemistry.[1] The major products of such syntheses are mixtures of isocyanate 'trimers' (**1** and **2**, see below) and 'dimers' (**3**).[1–3] Dimer **3** is the major product, especially at low isocyanate conversion. The composition of such mixtures is strongly dependent on the substrate, reaction conditions, and catalyst type. It was recently established that increasing the steric hindrance about the P atom considerably increases the uretdione selectivity of the phosphane catalyst in reactions with aliphatic isocyanates, such as the industrially important hexamethylene diisocyanate,[4] and a mechanism for this type of reaction has been proposed.[5]

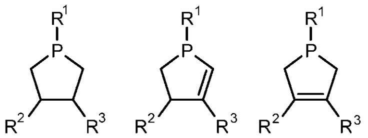


1
isocyanurate
'(symmetrical) trimer'

2
iminooxadiazinedione
'unsymmetrical trimer'

3
uretdione
'dimer'

In the course of this investigation the question arose, whether the migration of the phosphorus atom into the ring of a carbocycle would exert an influence on the selectivity of the reactions. The five-membered ring species **4**–**6** (see below), which are all readily accessible by the McCormack reaction,[6] optionally with subsequent hydrogenation (**4**), have been selected for this study.



4 **5** **6**

Surprisingly, the use of saturated species of type **4** (1-organyl-phospholanes) as catalysts[7] led to a complete reverse in the selectivity of the reaction, in favor of the formation of the isocyanate trimers, **1** and **2**. This is in contrast to earlier findings,[8] in which compounds of type **4**–**6** were claimed to be versatile carbodiimidization catalysts. Owing to the high activity of the corresponding *P*-oxides in carbodiimidization reactions,[9] it can be assumed that the findings mentioned in Ref. [8] can be attributed to partial air oxidation of the trivalent phosphorus species applied.

Compared to the saturated phosphacycles **4**, which are potent catalysts for isocyanate trimerization reactions,[7] the 2-unsaturated species **5** are considerably less active, but exhibit a very similar selectivity. The symmetrical species **6**, in total contrast to the other two members of the series, do not exhibit any catalytic activity with respect to isocyanates and instead react cleanly with two equivalents of isocyanate to effect the extrusion of 1,3-diene (Scheme 1).

To our knowledge, neither this type of reaction nor the resultant P-containing products, 1,4,2-diazaphospholidine-3,5-diones **7**, have been reported to date.[10] There are also only two preparative examples of the extrusion of a 1,3-diene from an unsaturated phosphacycle, such as **6**.[10a,b] In both cases, oxygen-containing nucleophiles (diethyl peroxide and methanol, respectively) induce the fragmentation.

Primary aliphatic isocyanates react smoothly without formation of P-containing side products (Scheme 1). The reac-

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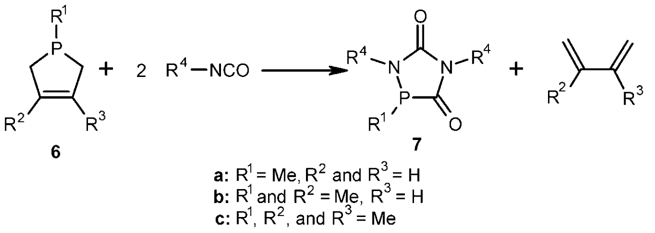
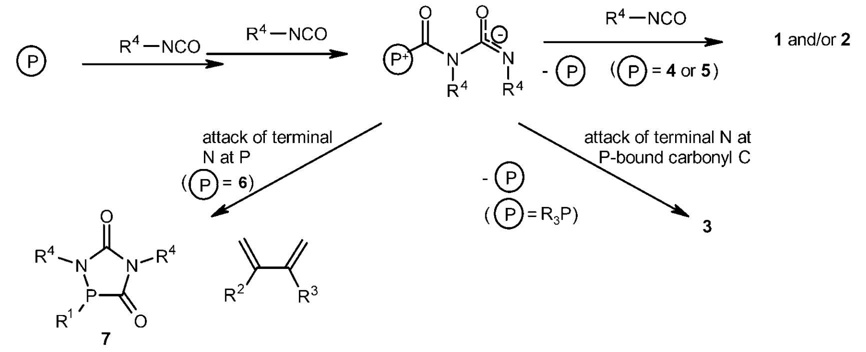


Scheme 1. Synthesis of 1,4,2-diazaphospholidine-3,5-diones **7** and concurrent extrusion of 1,3-dienes.

tivity of the phospholene moiety with a given isocyanate increases in the order **6a**<**6b**<**6c**. Longer alkyl or aromatic substituents at the P atom are tolerated.

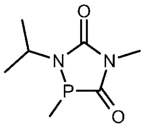
Depending on reaction conditions, minor amounts of isocyanate oligomers, especially carbodiimides and trimers, may be formed. This is especially true if **6** is contaminated with **5** and/or the corresponding phospholene oxides. However, the reaction can be used to obtain pure **5** from mixtures with the symmetrical isomer, if desired.



Scheme 2. Mechanistic proposal for isocyanate reactions of trivalent P compounds. Ⓟ = trialkylphosphane (R$_3$P) or **4**–**6**.

The reaction proceeds much more slowly with secondary isocyanates, cyclohexyl isocyanate reacting even slower than 2-propyl isocyanate, and does not proceed to a detectable degree with *tert*-butyl isocyanate.

On treating excess 2-propylisocyanate with 1-methyl-3-phospholene **6a** in the presence of methylisocyanate, the major reaction product was 1-(2-propyl)-2,4-dimethyl-1,4,2-diazaphospholidine-3,5-dione **8**, alongside the *N*,*N'*-dimethyl derivative **7** (R^1=R^4=Me; see the Supporting Information).



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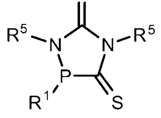
The formation of **8** is indicative of a stepwise mechanism for this reaction. The first step is undoubtedly the formation of an adduct, **6**–MeNCO, which is, unlike **6** itself, reactive enough to attack 2-propyl isocyanate in the second step. As it is highly unlikely that the P atom in the **6**–MeNCO attacks the second isocyanate (in this case 2-propyl isocyanate) the mechanism of this new reaction differs considerably from that proposed for the retro-McCormack reactions discussed in Ref. [10a,b], in which the formation of phosphorane-type activated species involving both oxygen nucleophiles in a P-centered intermediate is proposed (Scheme 2).

Notably, *P*-phenyl phospholenes also react cleanly in accordance with Scheme 1. This is surprising as no catalytic activity towards alkyl isocyanates is shown by aryl dialkyl phosphanes. This finding may help to afford a better understanding of the driving forces underlying the catalytic cycle in isocyanate oligomerization reactions; reversible adduct formation involving two or three isocyanate units, ring closure with formation of **1**–**3**, and simultaneous extrusion of catalyst or, in this case, 1,3-diene (Scheme 2).

The new type of reaction is not limited to isocyanates. Other heterocumulenes, isothiocyanates and carbodiimides, also form the appropriate phosphacycles; 1,4,2-diazaphospholidine-3,5-dithiones **9** and 1,4,2-diazaphospholidine-3,5-diimines **10**, respectively (see below). It must be noted at this point that the situation in the aromatic series (PhNCO, PhNCS, PhNCNPh) is not yet fully understood.



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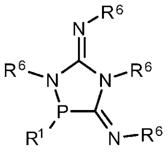

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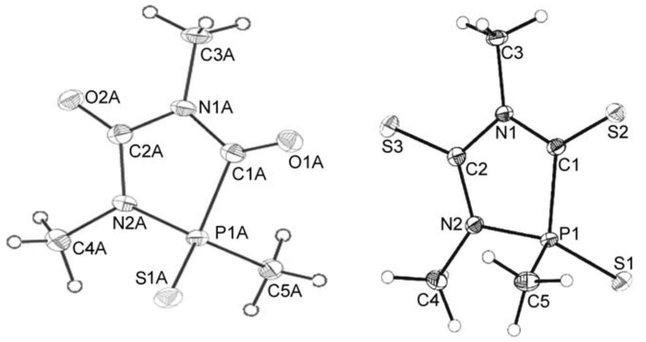
The new species exhibit the typical reactivity for trivalent P compounds and readily form *P*-oxides, *P*-sulfides, and quaternary onium salts.

The identity of the new compounds was unambiguously ascertained by multinuclear NMR spectroscopy, high-resolution mass spectrometry and X-ray crystal structure determination (see the Supporting Information).

As the title compounds are air-sensitive, the *P*-sulfides **11** (1,2,4-trimethyl-1,4,2-diazaphospholidine-3,5-dione 2-sulfide) and **12** (1,2,4-trimethyl-1,4,2-diazaphospholidine-3,5-dithione 2-sulfide) were chosen as suitable compounds for X-ray diffraction investigations (Figure 1). Compound **11** was shown to incorporate two slightly different molecules in the asymmetric unit, **11a** and **11b** (the latter is omitted from Figure 1 for clarity).

The N-C-N-C-units in the five-membered rings of **11** and **12** are almost planar (torsion angles: **11a**: −3.0(3)°; **11b**: 0.3(3)°; **12**: −1,15(6)°) with the P atom in a distorted



11a **12**

Figure 1. Molecular structures of **11a** and **12**. Thermal ellipsoids are set at 50 % probability.

tetrahedral environment with a maximum deviation from tetrahedral geometry in the N2-P-C1 bond angle (**11a**: 90.16(11)°, **11b**: 90.40(11)°; **12**: 89.81(6)°).

The chemistry of the new compounds will be the topic of further investigations. In spite of the interesting complexation behavior of structurally related 2*H*-1,2,4-diazaphospholes reported by Streubel and co-workers,[11] they may find applications as ligands in transition metal chemistry.

Acknowledgements

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Keywords: dienes · isocyanates · organocatalysis · phosphanes · phosphorus heterocycles

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