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RING ENLARGEMENT OF PHOSPHATRIAFULVENES WITH AZIDES TO 1*H*-2-IMINOPHOSPHETES[1]

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Abstract: The reaction of the mesitylphosphatriafulvene **2** with the azides **3a-k** yields the ring-enlarged 1*H*-2-iminophosphetes **6a-k**; the structure of **6j** was irrevocably established by an X-ray crystal structure analysis. In some cases, 1,3-diphosphetanes (**8b-e**) have been characterized as by-products.

Phosphatriafulvenes (**1A** ↔ **1B**, **Scheme 1**), first synthesized in 1989[2], represent phosphaalkenes with an increased electron density at the phosphorus atom and a lowered electron density in the olefinic increment (including the hydrogen atoms), as has been calculated by *ab initio* methods at the MP2/6-31+G* level.

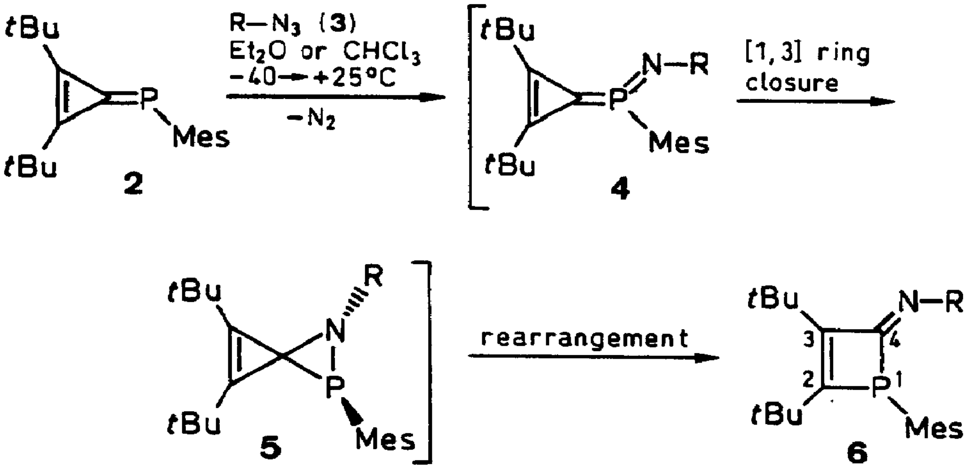
1A **1B**

SCHEME 1

This electronic configuration is supported by the extreme high-field shift of the ^{31}P NMR resonances (i.e. **2** δ = -23.2)[2,3] as well as by their reactivity. Electrophiles add to phosphorus[3,4] whereas nucleophiles primarily attack the cyclopropenyl moiety[5]. In this communication, we report on an unusual *Staudinger* reaction of **2** leading to the ring-enlarged 1*H*-2-iminophosphetes **6**.

When the phosphatriafulvene in diethyl ether or chloroform at -40°C is allowed to react with the azides **3a-k** in a ratio between 1:1 to 3:2 and the reaction mixture is then warmed to room temperature, the ^{31}P NMR spectrum shows one, two, or three signals, which could be assigned to the main product **6** or to mixtures of **6/7** and **6/7/8**, respectively; none of these chemical shifts is in the expected absorption range of the iminomethylenephosphoranes **4**[6]. Work up of the crude material by column chromatography (silica gel or aluminum oxide with diethyl ether/pentane, 1:2) yields the yellow title compounds **6a-k** (**Scheme 2**).

In full agreement with our proposed structures, products **6a-k** display ^{31}P NMR resonances (δ = -2.3 to 16.5) which are characteristic for $\lambda^3\sigma^3$-phosphorus. All ^{13}C-resonances of the four-membered ring skeleton are split by phosphorus couplings (C2: δ = 152.7-154.7, $^1J_{C,P}$ = 26.0-28.5Hz; C3: δ = 167.1-185.9, $^2J_{C,P}$ = 6.6-16.8Hz; C4: δ = 175.8-194.0, $^1J_{C,P}$ = 9.6-15.0 Hz). The final confirmation of the structure of the main reaction products was provided by an X-ray crystal structure analysis of **6j** (**Fig. 1**)[7].



4–6	a	b	c	d	e	f	g	h	i	j	k
R	C_6H_5	1-naphthyl	C_6H_4—Cl(3)	C_6H_4—Cl(4)	C_6H_4—NO_2(3)	C_6H_4—NO_2(4)	$C_6H_3(CH_3)_2$(2,6)	SO_2—C_6H_4—CH_3(4)	$PO(OC_6H_5)_2$	$CO_2C_2H_5$	CN

SCHEME 2

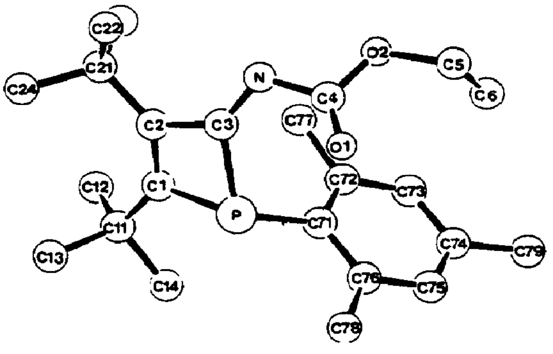
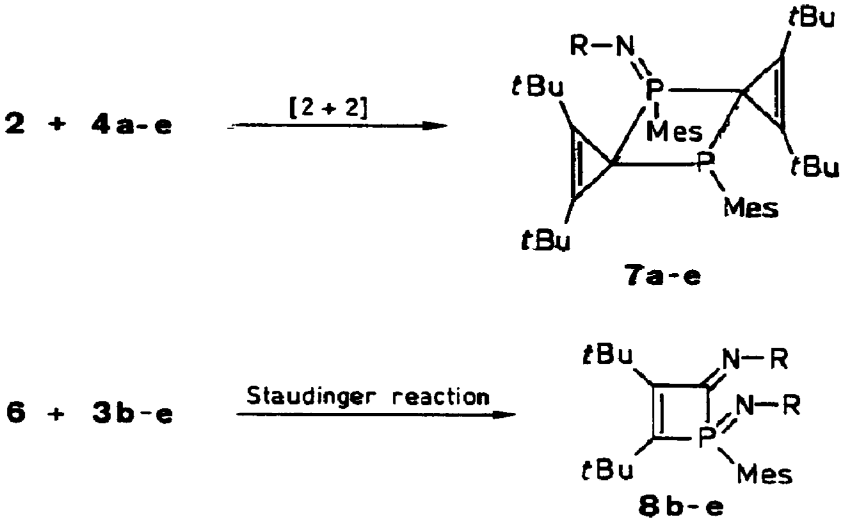


Fig. 1. Crystal structure of the 1*H*-2-iminophosphete **6j**. Selected bond lengths [Å] and angles [°]: P-C1 1.850(6), P-C3 1.848(6), P-C71 1.844(6), C1-C2 1.354(7), C2-C3 1.458 (7), C3-N 1.282(6); C1-P-C3 70.2(3), P-C1-C2 96.4(4), C1-C2-C3 98.3(5), C2-C3-P 92.9(4), C3-P-C71 107.2(3), P-C3-N 134.8(5).

The central ring system possesses a distorted rhombic geometry with normal P-C (1.850, 1.848 Å), C-C (1.458 Å), and C=C bond lengths (1.354 Å). This is in good agreement with structural investigations of comparable 1,2-dihydrophosphetes. The dihedral angle P-C1-C2-C3, which reflects the folding of the ring, is larger than that of all other representatives of this class of compounds[8]. Moreover, the crystal structure demonstrates clearly the *Z*-configuration at the C/N double bond. Since only one phosphorus NMR signal is observed for all members of the series (see above), it is most likely that **6a-i** and **k** have the same substituent arrangements around the C=N-bond.

Compounds **7a-e**, which are by-products of the reaction **2** + **3** → **6**, could not be purified satisfactorily either by crystallization or by column, high pressure liquid, or thin layer chromatography. The ^{31}P NMR spectrum of the crude material displays a characteristic AB-system with two doublets at δ = 55.5-58.5 and 41.6-47.7 having a $^{2}J_{P,P}$-coupling of 19.0-23.7 Hz. Further information on the structure of was obtained from a ^{15}N-tracer experiment (**2** + **3a**) which demonstrated that, in agreement with our structural proposals, only one phosphorus atom had been oxidized during the transformation (δ = 58.1 $^{1}J_{N,P}$ = 34.9 Hz). In addition, the spirocyclic compounds **7** possess a mirror plane, which makes the nuclei of the cyclopropenyl ring equivalent in the sense of the NMR. A [3+2] cycloaddition process between **2** and **4** can hence be discounted (**Scheme 3**).



SCHEME 3

The second by-product isolated from the reaction **2** + **3e** is the iminophosphorane **8e**, the final product of a subsequent *Staudinger* reaction. All NMR data of **8e** are in accord with the proposed structure, as can be seen from a comparison with the data of its precursor **6e**. Apart from this transformation the same compound has been obtained by the route **6e** + **3e** → **8e** + N_2, which provides further support for the suggested structure.

To obtain additional information about the reaction mechanism, *ab initio* calculations on all educts, intermediates, and products have been performed. A first attack of the azide to the phosphatriafulvene - leading to a triazene - was deduced by calculation of the transition states. It was found, that a [3+2] cycloaddition can almost certainly be excluded as the first step because no stationary point could be found for the 2*H*-2,3,4-triazaphospholene. In contrast, the 4*H*-2,3,4-triazaphospholene does represent a local minimum, but the transition state calculation resulted in a structure which was characterized as the transition state of the N_2-elimination of the *Staudinger* reaction. Hence it is most likely that the initial attack of the azide takes place at the lone-pair electrons of phosphorus, followed by elimination of N_2 to form an iminophosphatriafulvene. The existence of such an intermediate in our reaction is supported by the formation of **7** via [2+2] cycloaddition of **4** to **2**. The subsequent cyclisation to the spiro [2,2] azaphospholene **5** leads to the first connection between nitrogen and the ring carbon atom. Finally, a rearrangement involving a ring enlargement of the cyclcopropenyl moiety results in the formation of the 1*H*-2-iminohosphete **6**.

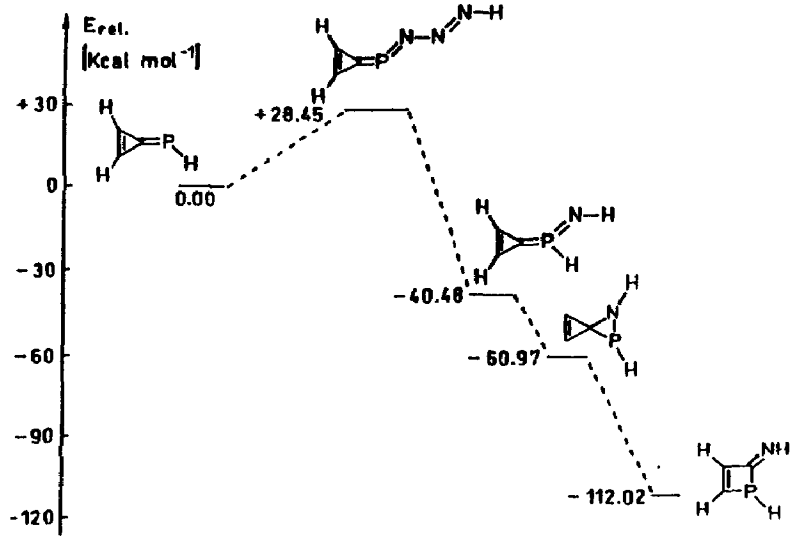


Fig. 2. Relative energies of the educt, the intermediates, and the product at the RHF/6-31G* level of theory, corrected for zero-point energy.

The reaction energies (Fig. 2) reveal endothermic behavior only for the first step (28.45 kcal/mol). All the following steps are exothermic and add up to a reaction enthalpy of ΔH = -112.02 kcal/mol. The required energy to form the *Staudinger* adduct shows the value of a typical activation barrier and is thus not expected to hinder the reaction sequence. Finally, this activation energy is in good accordance with the fact that the reaction can be frozen at a temperature of about -10°C, as was shown by dynamic ^{31}P NMR.

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