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BIS- AND TRIS(DIAZOMETHYL)PHOSPHANES - NEW BUILDING BLOCKS FOR THE SYNTHESIS OF PHOSPHORUS HETEROCYCLES[1]

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Abstract: The bis- and tris(diazomethyl)phosphanes **5** and **12**, obtained by electrophilic diazoalkane substitution of **4** or PCl_3 with lithiated **3**, are starting materials for complicated, heteroatom-substituted compounds. Thus, [3+2]-cycloadditions with the phosphaalkyne **8** and subsequent [1,5]-Tms shifts give rise to the phosphanes **10** and **13** which then condense with phosphorus, arsenic, antimony, silicon, or germanium halides to furnish heterocycles of the types **9**, **11**, or **15** with cleavage of chlorotrimethylsilane.

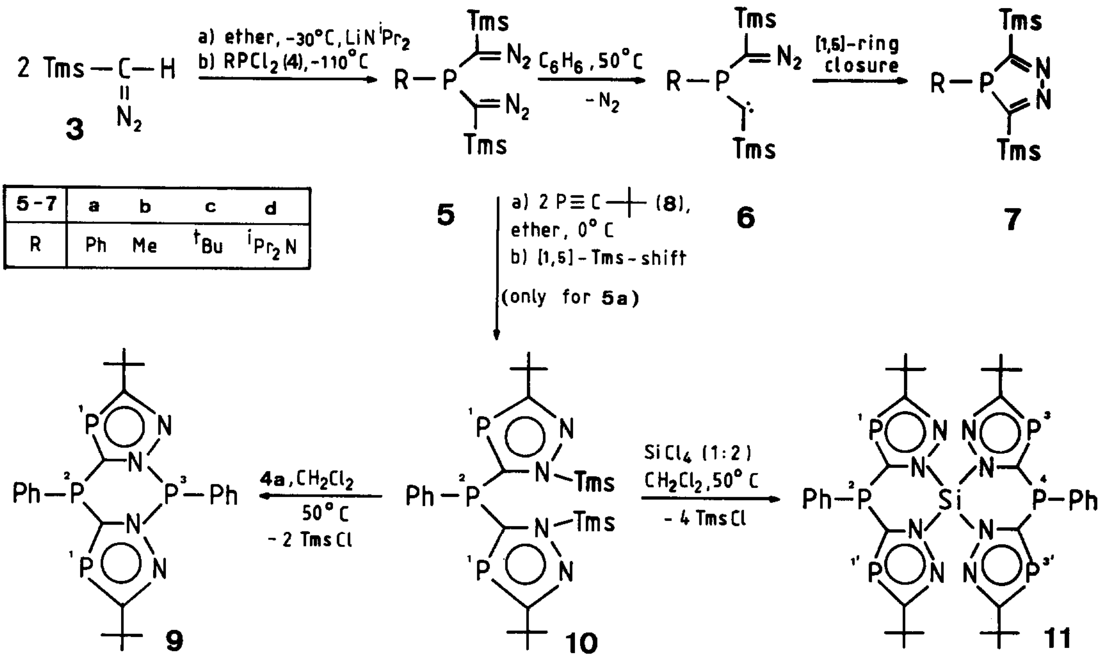
Donor-substituted diazo compounds are rare[2]: the first phosphino-substituted diazomethane was recently prepared from bis(diisopropylamino)chlorophosphane and diazo(trimethylsilyl)methyllithium[3]. Compounds of this type, in principle, open up a possibility to study the chemistry of the phosphinocarbenes **2A**. Here, the main question is whether these compounds exhibit ylide character according to **2B** or even behave as the $\lambda^5\sigma^3$-phosphaalkynes **2C**.

1 **2A** **2B** **2C**

In addition to this aspect, we were mainly interested to see whether the title compounds are also suitable for the preparation of phosphorus heterocycles.

When lithiated diazo(trimethylsilyl)methane (**3**)[5] is subjected to electrophilic diazoalkane substitution[6] with dichlorophosphanes **4a-d**, chromatographic work-up (Al_2O_3, pentane, -20 °C) of the crude reaction mixtures gives the bis(diazomethyl)phosphanes **5a-d** as yellow to orange oils in 30-60% yields. These products are characterized by diazo valency vibrations in the IR spectra [film, $\nu(C{=}N_2)$ = 2050-2040 cm^{-1}], diazo carbon atom signals in the ^{13}C-NMR spectra [C_6D_6, δ = 23.5-28.4 ppm, $^1J(C,P)$ = 76-87 Hz], and, finally, by strongly substituent-dependent signal patterns in the ^{31}P-NMR spectra (C_6D_6, δ = -39.0, -13.0. -14.9, and +32.6 ppm).

On thermal treatment, the bis(diazomethyl)phosphanes **5a-d** eliminate 1 mole of N_2 and are converted into the strongly air-sensitive, oily (with the exception of **7b**) 4H-1,2,4-diazaphospholes **7a-d**. Phosphinocarbenes **6** (or species of the type **2B** or **2C**) are assumed to be responsible for the ring closure. The phosphorus NMR resonances of **7a-d** are observed in the expected region (C_6D_6, δ = 61.5, 116.4, 82.9, 93.1 ppm)[7]. The C_s-symmetry of the heterocycles is apparent from the equivalence of the carbon atoms C-3 and C-5 in the ^{13}C-NMR spectrum of **7b** [C_6D_6, δ = 186.5 ppm, $^{1}J(C,P)$ = 52.9 Hz].

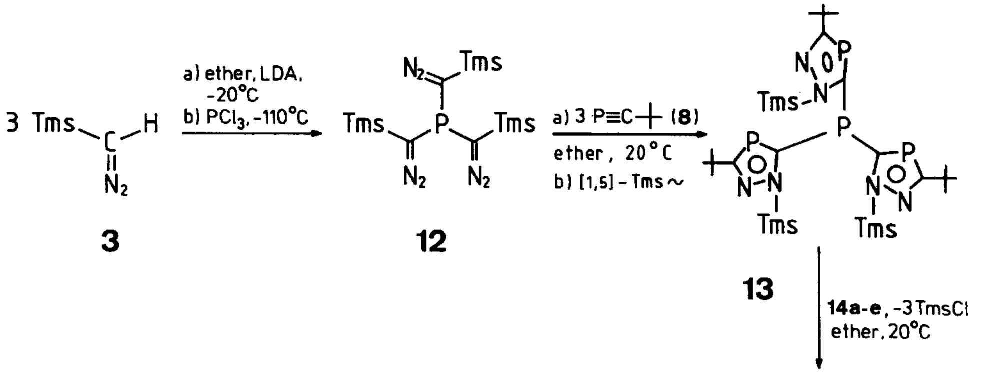


5-7	a	b	c	d
R	Ph	Me	^{t}Bu	^{i}Pr$_2$N

Compound **5a** undergoes a double, regiospecific [3+2]-cycloaddition with the phosphaalkyne **8**[8] and a subsequent [1,5]-sigmatropic Tms-shift gives rise to **10** [81% yield; colorless crystals; m.p. 132 °C; ^{31}P-NMR ($CDCl_3$): δ = 130.7 (d, $^{2}J(P,P)$ = 7.7 Hz, P-1), -42.1 ppm (t, $^{2}J(P,P)$ = 7.7 Hz, P-2)]. When **10** is allowed to condense with **4a**, an N-P-N bridge is formed smoothly to furnish **9** [76% yield; colorless crystals; m.p. 167 °C; ^{31}P-NMR ($CDCl_3$): δ = 121.1 (d, $^{2}J(P,P)$ = 37.4 Hz, P-1), 77.1 (s, P-3), -11.3 ppm (t, $^{2}J(P,P)$ = 37.4 Hz, P-2)][9].

An analogous condensation reaction of **10** with tetrachlorosilane results in the spiro-linked silicon heterocycle **11** (58% yield; colorless crystals; m.p. 225 °C). From molecular models, it can be seen that **11** has a twofold axis of rotation so that (in contrast to **9**) P-1/P-3' and P-1'/P-3 are magnetically equivalent; furthermore, P-2 and P-4 are chiral and thus also cannot be distinguished magnetically. These features are confirmed by the ^{1}H- and ^{31}P-NMR spectra ($CDCl_3$) as follows. Two signals at δ = 1.26 and 1.21 ppm are seen for the protons of the four t-butyl groups, the $\lambda^3\sigma^2$-phosphorus atoms P-1, P-1' as well P-3, P-3' appear as double doublets at δ = 129.9 and 128.8 ppm, respectively [^{2}J(P-2,P-1) = ^{2}J(P-4,P-3') = 116.6 Hz, ^{2}J(P-2,P-1') = ^{2}J(P-4,P-3) = 114.5 Hz, ^{4}J(P-1,P-1') = ^{4}J(P-3,P-3') = 4.3 Hz], and the $\lambda^3\sigma^3$-phosphorus atoms P-2 (= P-4) resonate at -30.9 ppm. The latter signals show the abovementioned splitting by the β-phosphorus atoms.

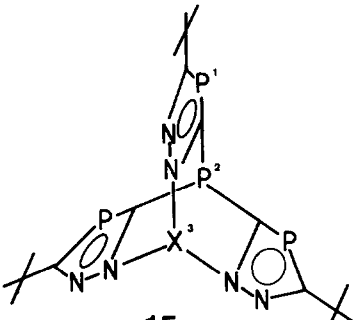
A comparable reaction sequence starting from PCl_3 gives access to a wide range of heteroatom-substituted bicyclic systems. Reaction of lithiated **3** with phosphorus trichloride in a molar ratio of 3:1 gives the tris(diazomethyl)phosphane **12** which is initially obtained as an oil but can be crystallized from pentane at -80 °C [orange-red crystals; m.p. 20 °C; IR(film): $\nu(C{=}N_2) = 2060$, 2030 cm^{-1}; ^{13}C-NMR (toluene-d_8): $\delta = 25.4$ (d, $^1J(C,P) = 82.7$ Hz, $C{=}N_2$), -1.5 ppm (q, $^1J(C,H) = 119.8$ Hz, CH_3); ^{31}P-NMR (C_6D_6): $\delta = -11.4$ ppm]. This unusual diazo compound is fairly stable at room temperature and reacts with three equivalents of the phosphaalkyne **8** via [3+2]-cycloaddition with subsequent Tms-shift to give the tris(1,2,4-diazaphospholyl)phosphane **13** [73% yield; colorless crystals; m.p. 108 °C; ^{31}P-NMR ($CDCl_3$): $\delta = 132.7$ (d, $^2J(P,P) = 12.4$ Hz, P-1), -55.4 ppm (q, $^2J(P,P) = 12.4$ Hz, P-2)].



3 **12** **13**

14,15	a	b	c	d	e
X	P	As	Sb	Si-Me	Ge-Me
m.p.[°C]	287	260	264[a]	210	254[a]
^{31}P-NMR[b] P-1	134.5[c]	123.0	120.0	131.9	123.2
P-2	-100.9	-95.5	-89.0	-110.4	-105.2
$[^2J(P,P)]$	[102.5]	[113.2]	[130.5]	[113.0]	[122.4]

[a] Decomposition. - [b] $CDCl_3$, δ in ppm, J in Hz. - [c] In addition: 167 (m, P-3), $^3J(P\text{-}1,P\text{-}3) = 8.5$ Hz, $^3J(P\text{-}2,P\text{-}3) = 15.6$ Hz.



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With equimolar amounts of phosphorus, arsenic, or antimony trichloride as well as methyltrichlorosilane or -germane (**14a-e**), **13** is converted to the heterosubstituted tris(diazaphospholo)bicycles **15a-e** with cleavage of three moles of chlorotrimethylsilane. The air-sensitive products are obtained as high-melting, colorless crystals after purification by evaporation of the reaction mixture and recrystallization from diethyl ether (-30 °C) or dichloromethane (-78 °C).

The conversion of **13** to **15** is clearly apparent in the ^{31}P-NMR spectra from the high field shift of the P-2 signal of $\delta = 33.6-55.0$ ppm[10]. At the same time, the $^{2}\underline{J}(P,P)$ coupling constants increase by a factor of up to about ten[11]. The carbon atoms adjacent to P-2 in the bicyclic skeleton absorb as multiplets in the region $\delta = 166.0-170.4$ ppm. In contrast to this, the signals of the t-butyl substituted carbon atoms in the diazaphosphole rings are, in relation, shifted to lower field [δ = 193.3-195.6 ppm, $^{1}\underline{J}(C,P) = 64.6-72.7$ Hz, $^{3}\underline{J}(C,P) = 9.0-10.7$ Hz].

All new compounds have been characterized by appropriate ^{1}H-NMR spectra, correct elemental analyses, and molecular ion peaks and fragmentation patterns in the mass spectra.

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REFERENCES AND NOTES

1. Unusually coordinated phosphorus compounds; part 28; for part 27, see: O. Wagner, G. Maas, M. Regitz, Angew. Chem. 1987, 99, in press; Angew. Chem. Int. Ed. Engl. 1987, 26, in press.
2. M. Regitz, G. Maas, Diazo Compounds - Properties and Synthesis, 1st. Edn., p. 567, Academic Press, Orlando/Florida, 1986.
3. A. Baceiredo, G. Bertrand, G. Sicard, J. Am. Chem. Soc. 1985, 107, 4781.
4. See, for example, H. Keller, G. Maas, M. Regitz, Tetrahedron Lett. 1986, 27, 1903; A. Baceiredo, A. Igau, G. Bertrand, M. J. Menu, Y. Dartiguenave, J. J. Bonnet, J. Am. Chem. Soc. 1986, 108, 7868; M. T. Nguyen, M. A. McGinn, A. F. Hegarty, J. Inorg. Chem. 1986, 25, 2185.
5. S. More, I. Sakoi, T. Aoyama, T. Shioiri, Chem. Pharm. Bull. 1983, 30, 2280.
6. Review: J. Fink, M. Regitz, Synthesis 1985, 569.
7. W. Rösch, U. Hees, M. Regitz, Chem. Ber. 1987, 120, 1645.
8. G. Becker, G. Gresser, W. Uhl, Z. Naturforsch. 1981, 36b, 16; improved procedure, see Ref.[7].
9. Compound **9** contains 15% of an isomer in which the two phenyl groups presumably have a cis-orientation.
10. Bond angles of about 90 ° are assumed to be responsible for this: D. Hellwinkel, W. Schenk, Angew. Chem. 1969, 81, 1049; Angew. Chem. Int. Ed. Engl. 1969, 8, 987.
11. For more information, see: S. Sørenson, H. J. Jakobson, Org. Magn. Res. 1977, 9, 101.

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