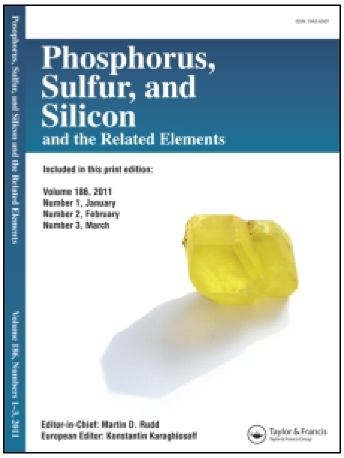

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Alkylidenephosphines and Diphosphetanes

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Alkylidenephosphines and Diphosphetanes

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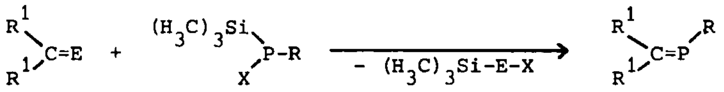
In studies of the reactivity and thermal stability of various alkylidenephosphines prepared from benzophenone and organylbis(trimethylsilyl)phosphines via a NaOH-catalyzed elimination of hexamethyldisiloxane (eq. 1a), detailed analyses of nmr-spectra and x-ray structure determinations prove the methyl derivative 1a to dimerize to an 1,3-diphosphetane (2a), whereas from the iso-propyl compound 1b the 1,2-diphosphetane 2b is obtained [1]. This observation confirms our hypothesis that the formation of 1,2- or 1,3-diphosphetanes is determined by the steric requirements of the substituent at phosphorus.

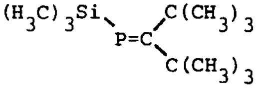


$$R^1_2C{=}E + (H_3C)_3Si(X)P{-}R \xrightarrow{-\ (H_3C)_3Si{-}E{-}X} R^1_2C{=}P{-}R$$

(eq. 1)

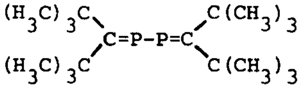
eq. 1a: $R^1 = H_5C_6$; E= O; X= $(H_3C)_3Si$
eq. 1b: $R^1 = (H_3C)_3C$; E= S; X= Li·2THF

Alkylidenephosphines with two bulky substituents at the carbon atom of the P=C moiety as e.g. two tert-butyl groups remain monomeric. These compounds are readily prepared from di(tert-butyl)thioketone and a lithium organyltrimethylsilylphosphide (eq. 1b). With lithium bis(trimethylsilyl)phosphide a mixture of [di(tert-butyl)methylidene]trimethylsilylphosphine (3), tris(trimethylsilyl)-phosphine, and the structurally characterized 2,3-diphospha-1,3-butadiene 4 is obtained.



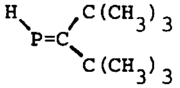
$(H_3C)_3Si{-}P{=}C(C(CH_3)_3)_2$

3 ;



$((H_3C)_3C)_2C{=}P{-}P{=}C(C(CH_3)_3)_2$

4 ;



$H{-}P{=}C(C(CH_3)_3)_2$

5

Treatment of compound 3 with methanol yields di(tert-butyl)methylidenephosphine 5 which dimerizes via a P-H addition of one molecule to the P=C group of a second one.

[1] G. Becker, B. Becker, W. Becker: Z. anorg. allg. Chem., in press.