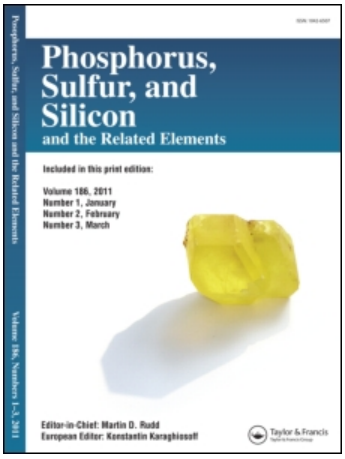

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INDUCTIVE AND STERIC EFFECTS IN THE STAUDINGER REACTION

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The sterically unhindered mode of the electrophilic addition of phenyl azide to trivalent phosphorus compounds and the inductive control in this initial step of the Staudinger reaction have been observed and discussed.

The oxidative imination of trivalent phosphorus compounds with phenyl azide, the Staudinger reaction[1] (Scheme 1), exhibits a peculiar feature. The rate constants of the initial association of the reactants, k_1, do not depend on mesomeric and steric interactions of the substituents with phosphorus, and are completely defined by their inductive influence on P^{III} atom.

$$R^1R^2R^3P: + PhN_3 \underset{}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1}}{R^1R^2R^3P{=}NN{=}NPh} \xrightarrow{k_2} \underset{\mathbf{2}}{R^1R^2R^3P{=}NPh} + N_2 \quad (1)$$

In the course of the subsequent decomposition of the intermediate phosphazide **1** to give nitrogen and imide **2**, the steric as well as electronic effects are operative.[2]

The Figure illustrates the inductive control in the electrophilic attack of phenyl azide on phosphorus atom in the primary step of the Staudinger reaction. Although in this series the size and the abilities of the radicals R^1, R^2 and R^3 to conjugate with P^{III} reactive site are varied in a rather wide range, the log k_1 values are linearly related only to the sums of σ_I parameters of the substituents at phosphorus (Eq. 2).[3]

$$\log k_1 = 2.274 - 5.656 \sum \sigma_I, \; r = 0.996, \; s = 0.08 \quad (2)$$

From the Eq. (2) the inductive characteristic of any new radical X can be calculated if the experimental kinetic parameter k_1 for the reaction of the corresponding compound R^1R^2PX and phenyl azide under the standard conditions is known.

$$\sum \sigma_I \pm 0.01 = 0.405 - 0.176 \log k_1 \quad (3)$$

This approach is particularly useful when the traditional pK_a-technique for determination of σ_I fails.[2]

The sterically unhindered nature of the initial electrophilic attack of phenyl azide on phosphorus in the Staudinger reaction becomes obvious if one compares the imination rates of trimethyl or

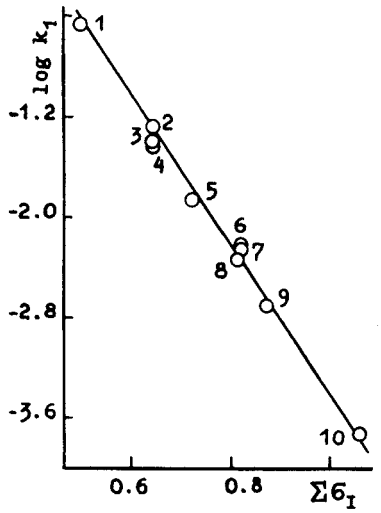


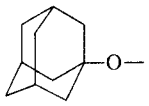
FIGURE 1 Plot of log k_1 versus $\sum \sigma_I$ parameters of the radicals R^1, R^2, R^3 for the reaction between $R^1R^2R^3P$ and PhN_3 in THF at 20°C. (1)–$(EtO)_2PMe$, (2)–$(EtO)_2PNMe_2$, (3)–$(EtO)_2PNEt_2$, (4)–$(EtO)_2PPh$, (5)–$(Me_2N)_2PF$, (6)–$(EtO)_2POPr$-*i*, (7)–$(EtO)_2POC_6H_{11}$-*c*, (8)–$(EtO)_3P$, (9)–$(MeO)_3P$, (10)–$(EtO)_2PF$.

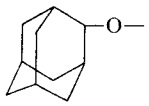
TABLE I

Rate constants[a] and activation parameters for the first step of the reaction between phosphites and phenyl azide in THF at 20°C

Phosphite	$k_1 \cdot 10^3$ M^{-1} sec^{-1}	E_a kcal/mol	$\Delta S^{\neq}$ e.u.
$(MeO)_3P$	1.97 ± 0.1	—	—
$(MeO)_2POAd\text{-}1$[b]	1.73 ± 0.03	12.7 ± 0.8	−29.9 ± 2.0
$(MeO)_2POAd\text{-}2$[c]	3.23 ± 0.05	14.4 ± 0.6	−22.9 ± 2.2
$(EtO)_3P$	4.48 ± 0.1	12.1 ± 0.4	−30.1 ± 1.3
$(EtO)_2POAd\text{-}1$	2.93 ± 0.03	13.2 ± 0.3	−27.0 + 1.0
$(EtO)_2POAd\text{-}2$	5.11 ± 0.08	13.2 ± 0.6	−25.9 ± 2.1

[a] All rates were determined a minimum of three times. The initial concentrations of the phosphites and phenyl azide were 0.06 and 0.96 M, respectively.

[b] 1-AdO = 

[c] 2-AdO = 

triethyl phosphite and their analogs having bulky 1- or 2-adamantoxyl groups, 1-AdO or 2-AdO (Table I).

The substitution of the MeO- or EtO-radical by the 1-AdO- or 2-AdO-group at the phosphorus atom does not change significantly the rate and the activation parameters of the first step. However, in the second step (Table II) which, as mentioned above, is rather sensitive to steric interactions, one 1-adamantoxyl group at phosphorus reduces the rate by a factor of 3–4. The retardation effect of two 1-AdO-radicals amounts to 150–220. In marked contrast, the 2-AdO-radical displays no influence on the kinetics of the second step in Scheme (1).

Using Eq. (3) and the rate data listed in Table I, the values of σ_I were calculated to be 0.31 and 0.26 for 1-AdO and 2-AdO, respectively.

In regard to the inductive electron-withdrawing character, both the adamantoxyl radicals are like the alkoxyl groups (the average σ_I-value 0.28).[4] It is possible that their mesomeric properties are also essentially the same. Therefore, the observed discrepancies in the kinetic behaviour of the 1-AdO- and 2-AdO-derivatives in the end imination step are probably due to the difference in the steric hindrance of phosphorus with sec.- or tert.-adamantoxyl radicals having two or six α-H atoms close to O—P bond, respectively. In the series examined the bulky 2-AdO-radical is almost equivalent, in a steric sense, to the variable alkoxyl substituents, MeO and EtO, i.e. in this case the screening ability of the radicals is not a function of their volume.

The preparation and spectral characterization of the adamantyloxy phosphorus species con-

TABLE II

Rate constants for the second step of the imination of phosphites and phosphonites with phenyl azide in THF at 20°C

Phosphorus substrate	$k_2 \cdot 10^3$ sec^{-1}	Phosphorus substrate	$k_2 \cdot 10^3$ sec^{-1}
$(MeO)_3P$	87.0 ± 2.4	$(EtO)_3P$	53.3 ± 1.8
$(MeO)_2POAd\text{-}1$	28.1 ± 0.5	$(EtO)_2POAd\text{-}1$	14.4 ± 0.5
$(MeO)_2POAd\text{-}2$	80.0 ± 2.4	$EtOP(OAd\text{-}1)_2$	0.24 ± 0.03
$(EtO)_2PPh$	154.0 ± 5.0	$(EtO)_2POAd\text{-}2$	66.2 ± 2.0
$PhP(OAd\text{-}1)_2$	1.05 ± 0.12		

TABLE III

Imination products of adamantyloxy phosphorus(III) compounds

Compound	Yield, %	Mp, °C (recrystn solvent)	Elemental analysis, P % cald. (found)
$(MeO)_2P(NPh)OAd\text{-}1$	82	91–92 (ethanol)	9.24 (9.19)
$(MeO)_2P(NPh)OAd\text{-}2$	81	57–58 (ethanol)	9.24 (9.26)
$(EtO)_2P(NPh)OAd\text{-}1$	83	66–68 (petrol ether)	8.52 (8.56)
$PhP(NPh)(OAd\text{-}1)_2$	75	199–201 (benzene)	6.17 (6.07)

cerned have been described.[5] In a typical preparative experiment a solution of phenyl azide (1–2 mmole) in dry benzene (1 ml) was added slowly to a solution of a phosphite (1 eq) in benzene (3 ml). After 5–6 hr stirring at 20°C, the solvent was removed and the residue was washed with petrol ether. Recrystallization provided the analytical samples (Table III). IR (KBr): 1355–1370 cm^{-1} (P=N). The oily imination products of $(EtO)_2POAd\text{-}2$ and $EtOP(OAd\text{-}1)_2$ partially undergo the structural rearrangement on distillation and will be described elsewhere.

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