Journal of Organometallic Chemistry, 333 (1987) C45–C47
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Kinetically and thermodynamically controlled interaction of organo-silicon (-boron) halides with lithium salts of acylphosphines. Influence of solvents and electrophilic catalysts

I.F. Lutsenko*, V.L. Foss, Yu.A. Veits, E.G. Neganova, A.A. Borisenko

Department of Chemistry, Lomonosov Moscow State University, Moscow, Lenin Hills, 117234 (U.S.S.R.)

(Received June 6th, 1987)

Abstract

Kinetically controlled interaction of $(R^1PCOR^2)Li$ with R_3SiCl in nonsolvating media gives *P*-silylated acylphosphines, which rearrange to *O-E* isomers. Direct formation of *O-Z* isomers was observed in solvating media with R_2BX and R_3SiX. Equilibria of *E/Z* isomers exist for B- or Si-derivatives of isobutyrylphosphines. Both isomers rearrange irreversibly to vinylphosphines.

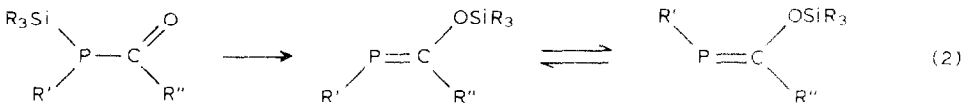
The discovery by Becker [1] of the rearrangement of *P*-silylsubstituted acylphosphines (I) to the more thermodynamically stable *O*-isomers (II) gave a powerful impulse to the development of two-coordinate phosphorus chemistry. However, data on kinetic control of the reaction of organosilicon halides with lithium salts of acylphosphines (reaction 1) are patchy and contradictory: the formation of both types I and II has been described [2,3].

$$\underset{\text{(III)}}{R_3SiCl + (R'PCOR'')Li} \xrightarrow[-\,LiCl]{} \underset{\text{(I)}}{R'P(SiR_3)COR''} \text{ or } \underset{\text{(II)}}{R'P{=}C(OSiR_3)R''} \qquad (1)$$

R = Me, Et, Pr; R′ and R″ = i-Pr, t-Bu. δ_P −4 to −28 ppm (for I), $^1J_{PSi}$ 28–35 Hz; δ_P 150–180 ppm (for II)

We studied reaction 1 in solvents with different solvating ability, because the role of solvent nature in alkylation of enolates is well known [4] (both salt III and enolate involve the ambident triad). It was shown, that reaction 1 (R = Me, Et; R′ = R″ = i-Pr) in petroleum ether at −40 °C leads rapidly and quantitatively to compounds I, i.e., the phosphorus atom of salt (III) is attacked selectively under conditions of kinetic control. The silylphosphines (I) obtained isomerize completely to phosphaalkenes (II) after 1–2 h at 20 °C. The quantitative formation of *E*-isomer (R = Et) was observed in absence of organosilicon chloride. In our opinion this fact proves the intramolecular migration of silicon (presence of organosilicon chloride accelerates both *E–Z* isomerization [5] (reaction 2) and conversion I → II).

0022-328X/87/$03.50

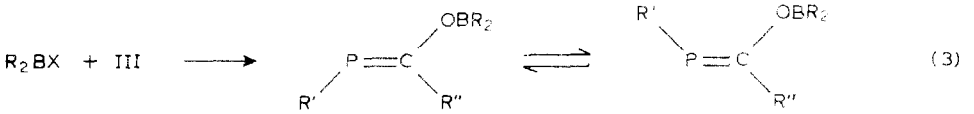


(2)

(*E*-II) (*Z*-II)

Kinetic control of reaction 1 at −40 °C (R′ = R″ = i-Pr) in dimethoxyethane (DME), and, particularly, in presence of benzo-12-crown-4 ether, is entirely different: the attack by electrophile is at the oxygen atom, *Z*-isomer predominating (over 90%, R = Et). The increase in steric hindrance in acylphosphine (R′ = t-Bu, R″ = i-Pr) gives exclusively the *Z*-isomer. Kinetic control inversion of the reaction 1, undoubtedly, is connected with deshielding of oxygen atom in salt III owing to solvation of lithium. Prevalence of *Z*-isomer depends upon the configuration of anion thus formed (steric and dipole repulsion is less in *trans (Z)* configuration, the latter is known for III when R′ = H, R″ = Mes [6]).

Recently obtained boron-substituted acylphosphines [5] are stable as *O*-isomers, so reaction 3 could be studied.



(3)

(*E*-IV) (*Z*-IV)

(R = alk, alk$_2$N)

Boron halides are more reactive than silicon chlorides. In light, of this fact, all attempts to detect compounds having P–B bond were unsuccessful. Irrespectively of solvent nature, only *O*-derivatives (boron analogs of compounds II) were detected in reaction 3, even when the reaction had not gone to completion. The formation of an *E*-*Z* isomer mixture, being near to equilibrium, was observed in different solvents, if R′ = R″ = i-Pr. However, an increase in steric hindrance (R′ = t-Bu, R″ = i-Pr, R = Et$_2$N) results in different kinetic products under different conditions: at −40 °C, the *E*/*Z* ratio in petroleum ether is 20 : 1, in DME it is about 1 : 1, and in presence of crown ether it is 1 : 20. Analogy with organosilicon compounds could be the basis for postulating that boron-phosphorus compound formation occurred during the interaction of salt III with organoboron halides in petroleum ether, and its rapid rearrangement to *O*-*E*-isomer, nevertheless we have no direct corroborations of this hypothesis now. The configuration of compounds II and IV results from the presence of three bulky groups R′, R″, and ER$_n$. Eventually, *trans* position of R′ and R″ substituents and steric repulsion of groups ER$_n$ and R′, disposing on one side of double bond, counteract each other. It is apparent, that the bulkier ER$_n$, the greater is the rate of *E*-isomer. However, it would be noted, that the volume of R″ exerts the predominant influence on equilibrium percentage of *E*-isomers of compounds II and IV. Indeed, according to ref. 7, compounds II (R″ = t-Bu, R′ = Me) contain only *Z*-isomers, despite the volume of alkyl substituent R′, and only in case of R′ = H both isomers exist [2]. When R″ = i-Pr, compounds II consist of mixtures of isomers even when a bulky t-butyl group is bonded to the phosphorus atom. The equilibrium ratio of isomers essentially depends on the volume of substituent R (at 20 °C 54% of *E*-isomer, 54% when R = Pr, 48% when R = Et and 20% when R = Me; at 150 °C the latter isomer

reaches 30%). Influence of the volume of R is appreciable in compounds containing $R' = R'' =$ i-Pr: at 20 °C if R = Me proportion of *E*-isomer is 35%, and when R = Et, it is 60%. The boron derivatives IV, and their silicon analogs, are stable only in *Z*-configuration when $R' = R'' =$ t-Bu, R = Alk, Alk_2N. Both isomers co-exist in compounds with $R'' =$ i-Pr, $R' =$ t-Bu: at 20 °C 15% *E* when $R = Et_2N$, 10% when $R = Me_2N$, when R = n-Alk only *Z*-isomer occurs. From these data, the percentages of the *E*-isomers for the same acylphosphines are less for the organoboron compounds IV than for their silicon analogs (II).

Structure determination was by NMR-spectroscopy; in accordance with ref. 8 the $J_{P=C-C}$ value are the most informative. For example, $J_{P=C-C}$ is twice as large for the *Z*-isomer than for the *E*-isomer. Other data are less informative, but for all the compounds investigated, the value of $J_{P=C}$ is about 15% greater for *Z*-isomers.

Phosphaalkenes II and IV are enough sufficiently stable to be isolated by vacuum distillation. However, when $R'' =$ i-Pr, they isomerize to vinylphosphines V (compounds of three-coordinate phosphorus) in presence of catalysts.

$$\underset{\text{(II, IV)}}{R'P{=}C(OER_n)CH(CH_3)_2} \rightarrow \underset{\text{(V)}}{R'PH{-}C(OER_n){=}C(CH_3)_2} \quad (4)$$

(E = Si, B)

Both electrophiles (R_nEX) and bases (salts III) catalyze this rearrangement, the former, and particularly iodosilanes, are more effective. Thus, isomerization does not depend on CH-acidity, whereas the analogous rearrangement [9], occurs only for phosphaalkenes containing acidic groups in R'' (isomerization was not observed even when $R'' = Ph_2CH$). We presume that the driving force for rearrangement 4 is the formation of the thermodynamically more stable isomers V, including strong B–O and Si–O bonds and containing no two-coordinate phosphorus.

Thus, a number of consecutive rearrangements I → *E*-II ⇌ *Z*-II → V and *E*-IV ⇌ *Z*-IV → V was observed. Thermodynamic stabilities of phosphaalkenes (II and IV) in comparison with vinylphosphines (V) are opposite to these of their nitrogen analogs – azomethines and enamines. This uniformity [10] is likely to be of general significance.

References

1 G. Becker, Z. Anorg. Allg. Chem., 423 (1976) 243
2 G. Becker, M. Rossler and W. Uhl, Z. Anorg. Allg. Chem., 473 (1981) 7
3 G. Becker, M. Rossler and E. Schneider, Z. Anorg. Allg. Chem., 439 (1978) 121
4 O.A. Reutov and A.L. Kurts, Usp. Khim., 46 (1977) 1964
5 Yu.A. Veits, E.G. Neganova and V.L. Foss, Zh. Obshch. Khim., 56 (1986) 715; Yu.A. Veits, E.G. Neganova, A.A. Borisenko, R.V. Brusov, V.L. Foss and I.F. Lutsenko, Dokl. Akad. Nauk SSSR, 292 (1987) 1072
6 G. Becker, H.M. Hartmann, A. Munch and A. Riffel, Z. Anorg. Allg. Chem., 517 (1984) 89
7 G. Becker and O. Mundt, Z. Anorg. Allg. Chem., 443 (1978) 53
8 G. Becker, O. Mundt and G. Uhl, Z. Anorg. Allg. Chem., 517 (1984) 89
9 O.I. Kolodiazhny and V.P. Kukhar, Zh. Obshch. Khim., 51 (1981) 2189
10 V.L. Foss, Yu.A. Veits, T.E. Chernikh and I.F. Lutsenko, Zh. Obshch. Khim. 54 (1984) 2670