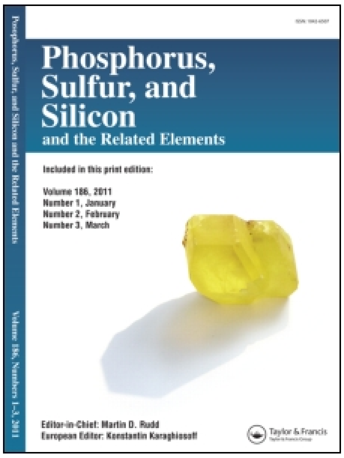
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Aspects of the Thio-Wittig-Reaction

Gerhard Erker; Regina Hock; Stefanie Wilker; Née Hillenbrand; Christian Laurent; Carsten Puke; Ernst-Ulrich Würthwein; Nicola C. Aust; Roland Fröhlich

To cite this Article Erker, Gerhard , Hock, Regina , Wilker, Stefanie , Hillenbrand, Née , Laurent, Christian , Puke, Carsten , Würthwein, Ernst-Ulrich , Aust, Nicola C. and Fröhlich, Roland(1999) 'New Aspects of the Thio-Wittig-Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 79 — 97

To link to this Article: DOI: 10.1080/10426509908546428

URL: http://dx.doi.org/10.1080/10426509908546428

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 79-97
Reprints available directly from the publisher
Photocopying permitted by license only

New Aspects of the Thio-Wittig-Reaction

GERHARD ERKER, REGINA HOCK, STEFANIE WILKER (née HILLENBRAND), CHRISTIAN LAURENT, CARSTEN PUKE, ERNST-ULRICH WÜRTHWEIN, NICOLA C. AUST and ROLAND FRÖHLICH

Organisch-Chemisches Institut, Universität Münster, Corrensstraße 40, D-48149 Münster, Germany

Treatment of phosphorus ylides with elemental sulfur, selenium or tellurium ("Staudinger-chalcogenation") leads to the formation of the respective chalcogenacarbonyls. The reaction of $Ph_3P=CH_2$ with thiobenzophenone gives a reactive thio-Wittig intermediate that exhibits a pronounced thio-betaine character in polar solvents. A thio-betaine is isolated from the reaction of $Et_3P=CHCH_3$ with $S=C(C_6H_4OCH_3)_2$ and characterized by an X-ray crystal structure analysis. The S···P separation in this gauche-betaine is 3.109(5) Å and the S-C-C-P dihedral angle amounts to 47.7(5)°.

Keywords: selenoketones; Staudinger-chalcogenation; thiaphosphetanes/thia-betaines

INTRODUCTION

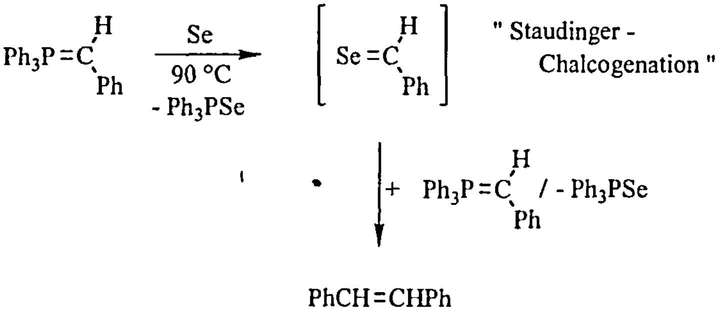
Thio-, seleno-, and tellurocarbonyl compounds exhibit MO-schemes that renders them more nucleophilic (higher n- and π-orbitals) and at the same time more electrophilic (lower π*-orbital) than their parent oxygen-containing carbonyl compounds. A close comparison of their orbital features also reveals that they may be much closer related to the corresponding alkenes than the $R_2C{=}O$ compounds[1]. This should lead to pronounced chemical differences in the $R_2C{=}X$ series on changing X from O to S, Se, and Te, and there have been many indications for these variations in chemical properties[2]. We will focus in this account on mechanistic aspects concerning cycloaddition reactions and, in some detail, the thio-Wittig reaction.

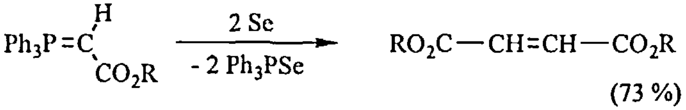
$R_2C{=}X$-PREPARATION BY THE "STAUDINGER-CHALCOGENATION"

A great variety of synthetic methods has been developed over the years for the selective preparation of thio-, seleno- or tellurocarbonyls, mostly involving various types of elimination reactions or cycloreversions[3]. An ingenious pathway was reported as early as in the year 1919 by H. Staudinger et al.. They have treated the phosphorus ylide $Ph_3P{=}CPh_2$, derived from Ph_2CN_2 by treatment with PPh_3, with elemental sulfur to cleanly obtain thiobenzophenone[4].

We, and independently of us K. Okuma et al., have utilized the analogous general reaction of phosphorus ylides with the elemental chalcogenes to generate reactive chalcogenocarbonyls[5]. Thus, the "Staudinger-chalcogenation" [5b] of $Ph_3P{=}CHPh$ with activated grey selenium led to the in situ generation of the reactive selenobenzaldehyde, which was trapped by the ylide starting material to form stilbene by means of a subsequent seleno-Wittig reaction.

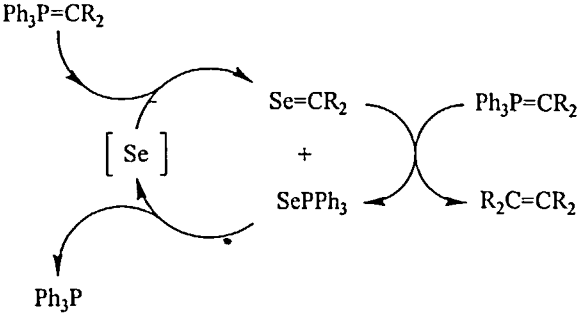
G. Erker, R. Hock (1987):



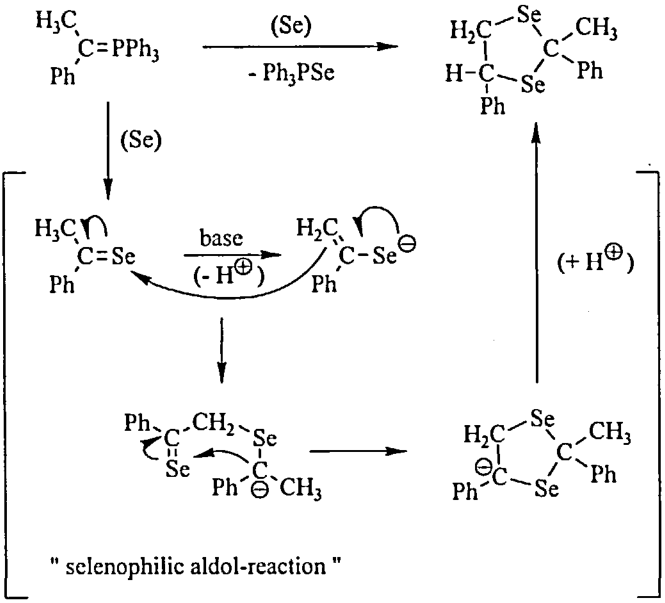


K. Okuma et al. (1987)

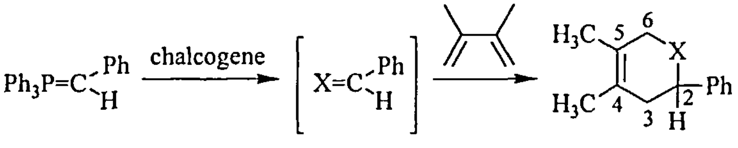
The resulting triphenylphosphinoselenide co-product of the seleno-Wittig reaction is not stable under the applied reaction conditions but tends to rapidly equilibrate with its components PPh_3 and selenium. This opened up a possibility for designing a catalytic variant of the "Staudinger cleavage" of ylides. In fact, it turned out that employing only ca. 10 mol% of elemental selenium (or alternatively of Ph_3PSe) was sufficient to cleave a variety of readily available ylides $Ph_3P{=}CR^1R^2$ to furnish the respective alkenes $R^1R^2C{=}CR^1R^2$ in reasonable yield (50 to 86%). 1,2-Disubstituted alkenes (R^1 = H, R^2 = $-C_2H_5$ to n-C_5H_{11}) were obtained in trans-/cis-ratios of ca. 85:15. The method is also suitable to prepare moderately strained tetrasubstituted alkenes[5b].



The "Staudinger-cleavage" may have its limitations when some readily enolized selenoketones are involved. In that case we have observed a series of more favorable reaction steps of a selenophilic aldol type that eventually results in the formation of a substituted 1,3-diselenolane product. This heterocycle is formed in high yield e.g. upon treatment of the ylide $Ph_3P{=}CPh(CH_3)$ with selenium at elevated temperatures.

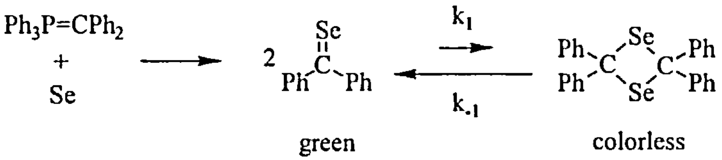


The intermediate occurrence of the chalcogenobenzaldehydes in the Staudinger-chalcogenation of $Ph_3P=CHPh$ was shown by trapping reactions carried out with reactive conjugative 1,3-dienes to yield the respective [4+2]cycloadducts[5,6]. Selenobenzaldehyde was trapped by in situ treatment with e.g. anthracene. It could be liberated from the cycloadduct by thermally induced retro [4+2]cycloaddition and transferred to e.g. 2,3-dimethylbutadiene to give 3,6-dihydro-4,5-dimethyl-2-phenyl-2*H*-selenapyran in good yield. Even the respective substituted dihydro-2*H*-tellurapyran could be obtained by this route[6]. Treatment of $Ph_3P=CHPh$ with elemental tellurium in the presence of 2,3-dimethyl-1,3-butadiene furnished the heterocyclic product from the telluro-Diels-Alder reaction in 11% yield along with a large amount of stilbene resulting from the "Staudinger-cleavage" of $Ph_3P=CHPh$ via the telluro-Wittig reaction of the in situ generated PhCH=Te reactive intermediate.



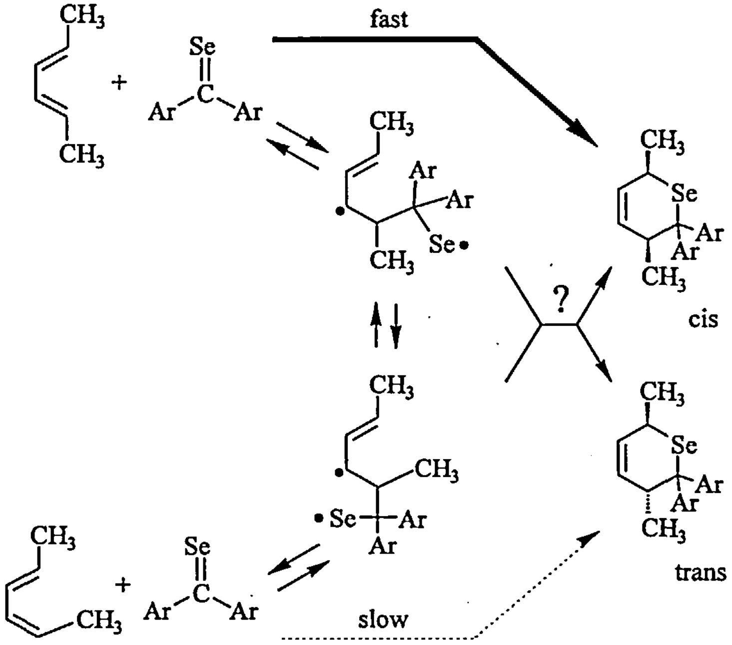
X = S, Se, Te

The Staudinger-chalcogenation reaction is well suited to prepare stable diarylselenoketones in a very easy way. The parent compound, selenobenzophenone, was obtained as a bright green monomer in e.g. toluene solution after treatment of $Ph_3P=CPh_2$ with activated grey selenium at elevated temperature[7]. Selenobenzophenone is characterized by UV-VIS absorptions at λ_{max} = 741 nm (ε = 80), 355 nm and 287 nm. Its ^{13}C NMR "carbonyl" resonance appears at δ 246 ppm. Upon concentration the thermodynamically less favored [2+2]cyclodimer precipitates from the solution and is recovered quantitatively (δ 129 ppm). Brought back into solution it is cleaved back to the monomer with a considerable Gibbs-activation barrier ($\Delta G^{\ddagger}$ (323K) = 24.4 kcal mol^{-1}; k_{-1} (cleavage) = $1.8 \cdot 10^{-4}$ s^{-1}; k_1 (dimerization of $Ph_2C{=}Se$) = $5.9 \cdot 10^{-6}$ l mol^{-1} s^{-1}), but this reaction can be accelerated considerably by proton catalysis.



Two of the diarylselenoketone [2+2]dimers were characterized by X-ray diffraction (Ar = Ph or p–C_6H_4F). Both show near to square planar central C_2Se_2 frameworks ($Ph_4C_2Se_2$: Se–C: 2.002(9) Å, Se–C–Se: 92.9(8)°, C–Se–C: 87.1(8)°).

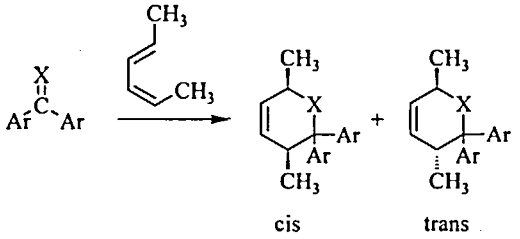
The mechanistic features of the thio- and seleno-Diels-Alder reactions were investigated by studying the [4+2]cycloadditions between a variety of differently substituted diarylthio- and selenoketones with the cis,trans- and trans,trans-2,4-hexadiene pair of conjugated diene stereoisomers[8]. The latter adds e.g. selenobenzophenone stereoselectively with overall retention of the stereochemical information to yield cis-3,6-dihydro-3,6-dimethyl-2,2-diphenyl-2*H*-selenapyran, the expected product of the concerted hetero-Diels-Alder reaction. In contrast, cis,trans-2,4-hexadiene reacts by complete loss of its stereochemical information and also yields the cis-3,6-dimethyl-substituted cycloadduct. Both reactions are kinetically controlled. It is known that cis,trans-2,4-hexadiene reacts ca. a thousand times slower in Diels-Alder reactions than the trans,trans-isomer[9]. We, therefore, have to assume that in this case a reversible addition of selenobenzophenone can very effectively compete with a concerted hetero-Diels-Alder reaction to give an intermediate that allows for the cis-/trans-isomerization of the conjugated diene[10]. The resulting trans,trans-2,4-hexadiene is then immediately used up in the very rapid stereospecific concerted [4+2]cycloaddition to give the cis-3,6-dimethyl-substituted heterocycle.



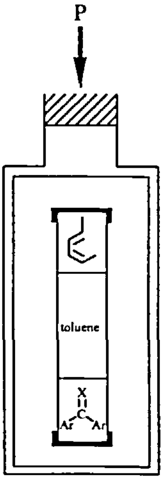
The essential intermediate of the diene isomerization reaction is very likely to have diradical rather than a dipolar character. This follows from only a marginal response of the pseudo-first order rate constant on the solvent polarity and of a Hammett ρ-value of close to zero[11].

Eventually, the concerted pathway of the [4+2]cycloaddition with cis,trans-2,4-hexadiene could be achieved by performing the reaction with diarylthio- and -selenoketones at high pressure[12]. Carrying out the reactions at 12 kbar, employing a special technique[8] that ensured that the bimolecular reaction did only take place when the high pressure regime was reached, gave predominantly the trans-3,6-dihydro-3,6-dimethyl-2,2-diaryl-2*H*-thia- and -selenapyran, the expected product of the concerted [4+2]cycloaddition reaction.

Stereochemistry of the thio- and seleno [4 + 2] Cycloaddition:
pressure dependence ($\Delta V^{\ddagger}$-effect):



Ar	1 bar: cis / trans X = S	Se	12 kbar: cis / trans X = S	Se
C_6H_5	>98:2	97:3	4:96	5:95
p-C_6H_4-F	>98:2	91:9	8:92	8:92
p-C_6H_4-OCH_3	>98:2	>98:2	-	16:84



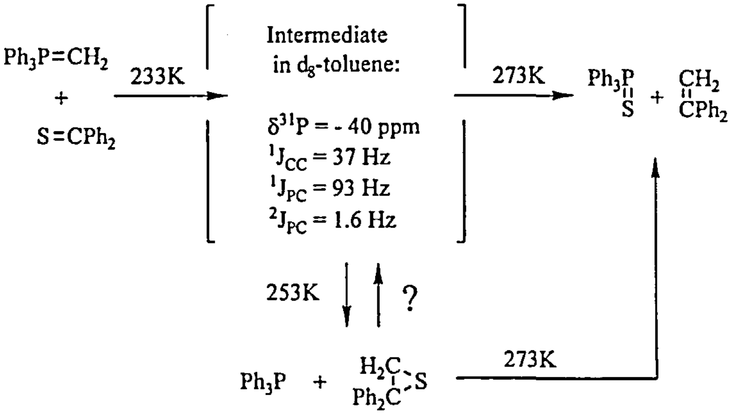
12 kbar
autoclave

THE THIO-WITTIG-REACTION

The examples of the "Staudinger-cleavage" of phosphorus ylides mentioned above have involved thio- and seleno-Wittig olefination reaction steps, respectively, along the overall CC-coupling pathway. This prompted us to investigate the mechanistic course of the thio-Wittig reaction (and its seleno-analogue) in some detail.

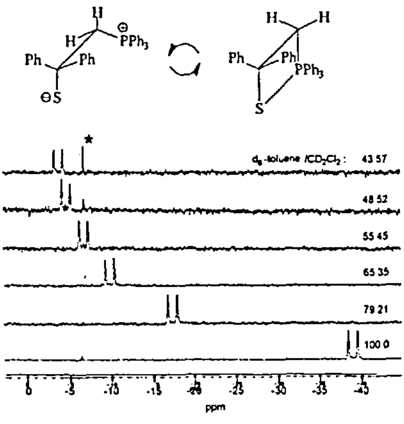
The mechanism of the Wittig olefination reaction starting from ordinary ketones or aldehydes appears to be widely established. It seems that in the majority of cases under typical salt-free conditions oxaphosphetanes are the essential intermediates, and that dipolar betaines are not involved[13]. A few oxaphosphetanes bearing stabilizing substituents have been characterized by X-ray diffraction[14], but NMR spectroscopy, especially of the ^{31}P nucleus, has remained the most essential analytical tool for the low-temperature detection and characterization of the intermediately formed reactive oxaphosphetanes[15]. As a reference for the mechanistic thio-Wittig study, that will be described below, we have generated the respective oxaphosphetane system by treatment of $Ph_3P={}^{13}CH_2$ with $O={}^{13}CPh_2$ (both reagents singly isotopically ^{13}C labelled for the NMR analysis) at 243K. The oxaphosphetane is rapidly and exclusively formed, and it is stable at that temperature. It shows a ^{31}P NMR resonance at δ -68.5 ppm which indicates the presence of the pentacoordinate phosphorus center. The four-membered ring connectivity is shown by the respective coupling constants of $^{1}J_{CC} = 33$ Hz, $^{1}J_{PC} = 86$ Hz, $^{2}J_{PC} = 14$ Hz. At 273K the 2,2,2,4,4-pentaphenyloxaphosphetane rapidly decomposes to give the final Wittig-products 1,1-diphenylethene and triphenylphosphineoxide.

The reaction between thiobenzophenone and the ylide methylenetriphenylphosphorane was carried out in d_8-toluene solution and followed directly by NMR spectroscopy[16]. Combinations of suitably ^{13}C-labelled materials were used to secure the atom connectivities of intermediates and products. At 233K a single intermediate was formed that was stable at the low temperature. It exhibits characteristic spectroscopic features that point to some thiaphosphetane character. Especially the observed ^{31}P NMR chemical shift of δ -40 ppm would be in accord with such an interpretation. At 253K this first intermediate decomposes to give the products 2,2-diphenylthiirane[17] and triphenylphosphine. Further temperature increase then lets these intermediate products again disappear to eventually yield the final thio-Wittig olefination products 1,1-diphenylethene and triphenylphosphinesulfide.



We attempted to study the corresponding seleno-Wittig reaction (i.e. $Se{=}^{13}CPh_2$ + $Ph_3P{=}^{13}CH_2$) in a similar way. But due to solubility problems, probably because of [2+2]dimer precipitation at low temperature (see above), the solvent had to be changed from d_8-toluene to d_2-dichloromethane. An intermediate of the seleno-Wittig reaction was observed with difficulties in low concentration, but it showed a ^{31}P NMR feature in the typical tetracoordinated phosphonium range[18] at ca. +11 ppm instead of the expected pentacoordinated ^{31}P NMR signal at a strongly negative δ-value. A thorough experimental investigation then revealed that this drastic change was probably not intrinsically caused by changing the chalcogene (here from sulfur to selenium) but that it was very likely due to a very pronounced solvent effect[19].

This was revealed when successive small portions of CD_2Cl_2 were added to a d_8-toluene solution of the alleged thiaphosphetane intermediate at low temperature. The chart below shows the obtained ^{31}P NMR spectra of a typical series of experiments using the example of the intermediate obtained from the $Ph_3P{=}^{13}CH_2$ + $Ph_2C{=}S$ addition. There is a continuous increase of the ^{31}P NMR chemical shift observed



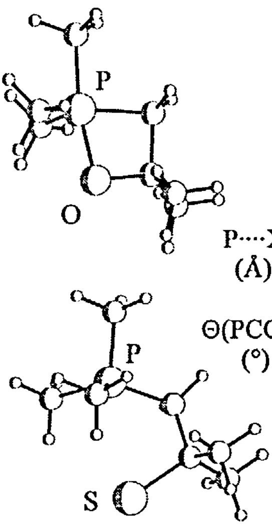
	at: 243K	
	d_8-toluene	CD_2Cl_2
$\delta^{31}P$	-40	+1
$\delta^{13}CH_2$	65	52
$\delta^{13}CPh_2$	50.5	50 4
$^1J_{CC}$	37	38
$^1J_{PC}$	94	82
$^2J_{PC}$	1.6	1.6

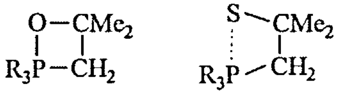
Chart 1

with increasing the dichloromethane concentration. The S–C–C–P connectivity is not principally affected by this change. Some of the coupling constants and ^{13}C NMR chemical shifts are slightly altered. The addition of other polar solvents has a similarly pronounced effect.

Thus, this may mean that there is a possibly continuous change of the very nature of the thio-Wittig intermediate being observed to take place changing from dominating thiaphosphetane character in an unpolar solvent to predominating betaine character in a more polar solvent. We have proposed to describe such a transition, if it were not taking place by a conventional shifting of a rapid equilibrium, by a new symbol, a pair of curved arrows.

A theoretical investigation[19] has also revealed major differences between the structural properties of the essential intermediates of the Wittig-reactions between $Me_3P=CH_2$ with $Me_2C=O$ or $Me_2C=S$ (see chart 2). The calculations produced an oxaphosphetane structure in the oxygen-containing system, containing the expected planar four-membered heterocyclic ring system. The calculated structure of the intermediate of the corresponding thio-Wittig reaction is quite different. The S–C–C–P core of the molecule is not planar but adopts a near to gauche arrangement of the S–C and P–C vectors along their connecting newly formed C–C single bond (dihedral angle ca. 40°), and the P···S separation is very large (ca. 3.1 Å). Although this is still within the sum of P and S van der Waals radii, the structure of this calculated thio-Wittig intermediate is close to what can be regarded a betaine-type structure. It may be described as a "gauche-betaine". Decreasing the electron-donation of the three bystanding substituents at phosphorus should result in a decrease of the phosphonium character and thus might lead to a continuous shifting from a gauche-betaine towards a thiaphosphetane-type structure. This is indeed observed. Going from a Me_3P to a H_3P derived system decreased both the S···P separation and S–C–C–P dihedral angle considerably. Eventually $(CF_3)_3P$ incorporation resulted in a planar system with only a slightly elongated P–S bond, according to this calculation[19].



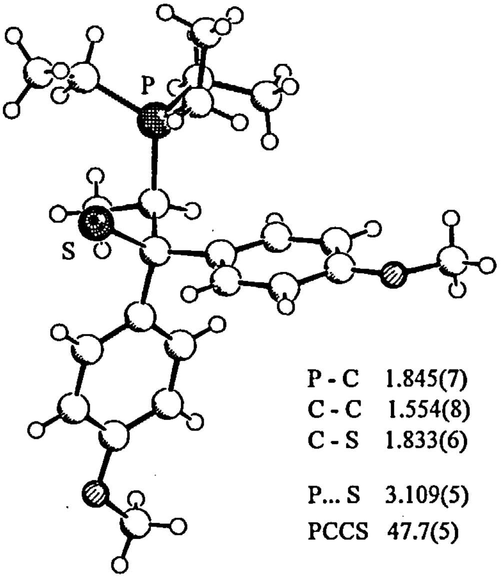


	$(CH_3)_3P$	$(CH_3)_3P$	H_3P	$(CF_3)_3P$
P····X (Å)	1.826^{+} (1.830^{*})	3.140^{+} (3.449^{*})	2.535^{+} (2.932^{+})	2.243^{*} (2.467)
Θ(PCCX) (°)	0^{+} (0^{*})	39.1^{+} (51.4^{*})	26.1^{+} (36.1^{+})	0^{*} (0.5)

$^{+}$ RHF/6-31+G*//6-31+G*
* RHF/6-31G*//6-31G*
(2 H_2O molecules added in the calculation)

Cart 2 Oxa-/Thiaphosphetane: ab initio Calculation
(E.-U. Würthwein, N. C. Aust)

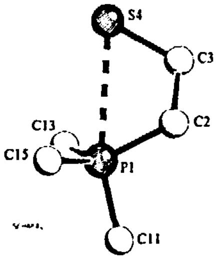
Adjusting the substituents at phosphorus has a marked influence on the structure and the stability of the CC-coupled thio-Wittig intermediate. I. V. Borisova et al. had shown that treatment of the ylide $(C_2H_5)_3P=CHCH_3$ with $S=C(C_6H_4NMe_2)_2$ produced a rather stable CC-coupled thio-Wittig intermediate that was thought to possess a betaine structure[20]. The major argument for this interpretation was the observed positive ^{31}P NMR chemical shift (δ +25 ppm in d_5-pyridine) that was in the typical phosphonium range[18]. We have treated $(C_2H_5)_3P{=}CHCH_3$ with $S{=}C(C_6H_4OCH_3)_2$ to yield the analogous thio-Wittig intermediate [S-CAr$_2$-CHMe-PEt$_3$; ^{31}P NMR: δ +21 ppm in d_8-THF, $^{1}J_{PC}$ = 71 Hz, $^{3}J_{PC(ipso\text{-}Ar)}$ = 0 and 14 Hz]. In this case single crystals of the addition product were obtained that have allowed for its characterization by an X-ray crystal structure analysis[19].



P - C	1.845(7)
C - C	1.554(8)
C - S	1.833(6)
P... S	3.109(5)
PCCS	47.7(5)

Figure 1 Molecular structure of the "gauche-betaine" obtained from the reaction of the ylide $(C_2H_5)_3P{=}CHCH_3$ with $S{=}C(C_6H_4OCH_3)_2$

A view of the molecular geometry of the $(C_2H_5)_3P{=}CHCH_3$ addition product to $S{=}C(C_6H_4OCH_3)_2$ is given in Figure 1. It shows that a gauche-betaine has been formed that is structurally very similar to the calculated structure of the $Me_3P{=}CH_2$ + $S{=}CMe_2$ thio-Wittig intermediate (see above). The central framework deviates markedly from planarity. The S–C–C–P dihedral angle amounts to 47.7(5)°, and the S···P separation is very large at 3.109(5) Å. Both the S–C (1.833(6) Å) and P–C (1.845(7) Å) bonds are in the single bond range, as is the newly formed carbon-carbon bond (1.554(8) Å).



P1 is located 0.41Å beneath the C2-C13-C15 plane

S4····P1	3.109(5)Å
S4····P1-C11	163.9°
C13-P1-C15	111.2°
C2-P2-C15	116.4°
C2-P1-C13	117.6°
C11-P1-C2	104.1°
C11-P1-C13	106.0°
C11-P1-C15	98.7°

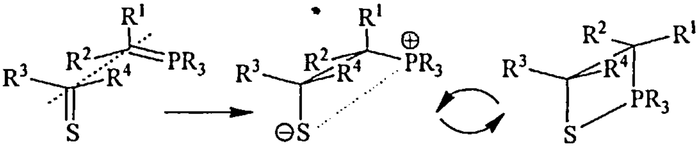
(the sum of S + P van der Waals radii is ca. 3.6Å)

Figure 2 A view of the core of atoms of the $(C_2H_5)_3P{=}CHCH_3$ + $S{=}C(C_6H_4OCH_3)_2$ gauche-betaine intermediate.

A close inspection of the central core of atoms of this structure (see Figure 2) shows that the coordination geometry around phosphorus is markedly distorted from trigonal-bipyramidal toward a tetrahedral phosphonium type. This compound thus appears to represent the first example of a structurally characterized betaine-type intermediate in a Wittig-olefination reaction[21], although it must be stressed that the large P···S separation of this gauche-betaine is still within the sum of the van der Waals radii of these elements, which leaves room for a small coordinative or, more likely, electrostatic stabilizing interaction.

CONCLUSIONS

The "Staudinger-chalcogenation", i.e. the selective cleavage of the ylidic phosphorus-carbon bond by treatment of $R_3P{=}CR^1R^2$ reagents with elemental sulfur, selenium or tellurium, has turned out to be a suitable method for generating thio-, seleno- or tellurocarbonyl compounds. In many cases very reactive $R^1R^2C{=}X$ or $R^1CH{=}X$ compounds were generated in this way in situ and trapped – either by means of [4+2]cycloadditions with added conjugated diene scavengers or by a subsequent chalcogeno-Wittig reaction with the starting ylide to yield the olefin coupling products. In some cases the Staudinger-chalcogenation of ylides can be used for the preparation of stable diarylselenoketones and their [2+2]cyclodimers. Our mechanistic study of the $Ph_3P{=}CH_2$ + $S{=}CPh_2$ reaction has shown that the thio-Wittig reaction proceeds through a reactive intermediate that exhibits characteristics different from those of the established oxaphosphetane intermediates of the common Wittig olefination reaction of ordinary ketones or aldehydes. It is likely that weakly internally stabilized gauche-betaine intermediates can be formed in the thio-Wittig reaction – a first example of this class of compounds was characterized by X-ray diffraction in the course of this study – and that there may be a continuous transition between gauche-betaines and chalcogenaphosphetane-type structures, depending on the external conditions applied and the substituents attached at the central framework.



ACKNOWLEDGEMENTS

Financial support by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen is gratefully acknowledged.

References

[1] V. P. Rao, J. Chandrasekhar, and V. Ramamurthy, *J. Chem. Soc. Perkin, Trans. II*, 647 (1988). E. Vedejs, D. A. Perry, K. N. Houk, and N. G. Rondan, *J. Am. Chem. Soc.*, **105**, 6999 (1983).

[2] See e.g.: P. Metzner, D. R. Hogg, W. Walter, and J. Voss, in *Organic Compounds of Sulfur, Selenium, and Tellurium;* edited by D. R. Hogg (The Chemical Society: London, 1977), Vol. 4, p. 124. J. Voss, in *Houben-Weyl, Methoden der Organischen Chemie;* edited by D. Klamann (Georg Thieme, New York, 1985), Bd. E 11, p. 188. C. Paulmier, in *Selenium Reagents and Intermediates in Organic Synthesis;* edited by J. E. Baldwin (Pergamon, Oxford, 1986), p. 58. K. A. Jensen and A. Kjaer, in *The Chemistry of Organic Selenium and Tellurium Compounds;* edited by S. Patai and Z. Rappoport (Wiley, New York, 1986), Vol. 1, p.1. F. S. Guziec, Jr., in *The Chemistry of Organic Selenium and Tellurium Compounds;* 1987, Vol. 2, p. 215. F. S. Guziec, Jr., in *Organoselenium Chemistry,* edited by D. Liotta (Wiley, New York, 1987), p. 277. E. Schaumann, in *The Thiocarbonyl Group;* in *The Chemistry of Double-bonded Functional Groups,* edited by S. Patai (Wiley, New York, 1989), Vol. 2, p. 1269.

[3] For selected examples see e.g.: T. G. Back, D. H. R. Barton, M. R. Britten-Keley, and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975); *J. Chem. Soc., Perkin Trans 1,* 2079 (1976). E. R. Cullen, F. S. Guziec, Jr., C. J. Murphy, T. C. Wong, and K. K. Andersen, *J. Am. Chem. Soc.*, **103,** 7055 (1981); *J. Chem. Soc., Perkin Trans 2,* 473 (1982). A. Ishii, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **61,** 861 (1988). R. Okazaki, N. Kumon, and N. Inamoto, *J. Am. Chem. Soc.,* **111,** 5949 (1989). G. W. Kirby and A. N. Tretheway, *J. Chem. Soc., Chem. Commun.,* 1152 (1986); *J. Chem.*

Soc., Perkin Trans 1, 1933 (1988). G. A. Krafft and P. T. Meinke, *J. Am. Chem. Soc.*, **108**, 1314 (1986); *Tetrahedron Lett.*, **28**, 5121 (1987) ; *J. Am. Chem. Soc.*, **110**, 8671, 8679 (1988). M. Segi, T. Nakajima, S. Suga, S. Murai, I. Ryn, A. Ogawa, and N. Sonoda, *J. Am. Chem. Soc.*, **110**, 1976 (1988). R. Okazaki, N. Kumon, and N. Inamoto, *J. Am. Chem. Soc.*, **111**, 5949 (1989). M. Minoura, T. Kawashima, and R. Okazaki, *J. Am. Chem. Soc.*, **115**, 7019 (1993).

[4] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919). H. Tokunaga, K. Akiba, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **45**, 506 (1972).

[5] a) K. Okuma, J. Sakata, Y. Tachibana, T. Honda, and H. Ohta, *Tetrahedron Lett.*, **28**, 6649 (1987). K. Okuma, Y. Komiya, I. Kaneko, Y. Tachibana, E. Iwata, and H. Ohta, *Bull. Chem. Soc. Jpn.*, **63**, 1653 (1990). b) G. Erker, R. Hock, and R. Nolte, *J. Am. Chem. Soc.*, **110**, 624 (1988). R. Hock, S. Hillenbrand, G. Erker, C. Krüger, and S. Werner, *Chem. Ber.*, **126**, 1895 (1993). R. Fröhlich, M. Grehl, S. Wilker, G. Erker, P. Mazerolles, and C. Laurent, *Z. Naturforsch.*, **49b**, 1397 (1994).

[6] G. Erker and R. Hock, *Angew. Chem.*, **101**, 181 (1989); *Angew. Chem. Int. Ed. Engl.*, **28**, 179 (1989).

[7] G. Erker, R. Hock, C. Krüger, S. Werner, F.-G. Klärner, and U. Artschwager-Perl, *Angew. Chem.*, **102**, 1082 (1990); *Angew. Chem. Int. Ed. Engl.*, **29**, 1067 (1990).

[8] S. Wilker and G. Erker, *J. Am. Chem. Soc.*, **117**, 10922 (1995).

[9] R. Sustmann, M. Böhm, and J. Sauer, *Chem. Ber.*, **112**, 883 (1979). H. D. Scharf, H. Plum, J. Fleischhauer, and W. Scheker, *Chem. Ber.*, **112**, 862 (1979).

[10] K. Gollnick and A. Griesbeck, *Tetrahedron Lett.*, **24**, 3303 (1983). K. E. O'Shea and C. Foote, *J. Am. Chem. Soc.*, **110**, 7167 (1988).

[11] a) R. Huisgen, *Acc. Chem. Res.*, **10**, 117 (1977); *Pure Appl. Chem.*, **52**, 2283 (1980). b) S. S. Friedrich; L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **55**, 944 (1970). W. A. Pryor, D. F. Church, F. Y. Tang, and R. H. Tang, in *Frontiers of Free Radical Chemistry*, edited by W. A. Pryer (Academic Press, New York, 1980), p. 355. D. Forrest, K. U. Ingold, and D. H. R. Barton, *J. Phys. Chem.*, **81**, 915 (1977). J. Kamphuis, P. D. J. Grootenhuis, and H. J. T. Bos, *Tetrahedron Lett.*, **24**, 1101 (1983).

[12] *Organic High Pressure Chemistry*, edited by W. J. le Noble (Elsevier, Amsterdam, 1988). F.-G. Klärner, *Chem. Unserer Zeit*, **23**, 53 (1989). R. van Eldik, T. Asano, and W. J. le Noble, *Chem. Rev.*, **89**, 549 (1989). N. S. Isaacs, *Tetrahedron*, **47**, 8463 (1991).

[13] E. Vedejs and M. J. Peterson, in *Advances in Carbanion Chemistry*, edited by V. Snieckus (JAI Press, Greenwich, CT, 1996), Vol. 2, p. 1–85, and references therein. But see also: J. P. Begue, D. Bonnet-Delpon, D. Mesurer, G. Nee, and S. W. Wu, *J. Org. Chem.*, **57**, 3807 (1992).

[14] T. Kawashima, K. Kato, and R. Okazaki, *J. Am. Chem. Soc.*, **114**, 4008 (1992); *Angew. Chem.*, **105**, 941 (1993); *Angew. Chem. Int. Ed. Engl.*, **32**, 869 (1993) and references therein. Review: T. Kawashima and R. Okazaki, *Synlett*, 600 (1996).

[15] E. Vedejs, K. A. J. Snoble, *J. Am. Chem. Soc.*, **95**, 5778 (1973). E. Vedejs, G. P. Meier, and K. A. J. Snoble, *J. Am. Chem. Soc.*, **103**, 2823 (1981). B. E. Maryanoff, A. B. Reitz, M. S. Mutter, R. R. Inners, H. R. Almond Jr., R. R. Whittle, and R. A. Olofson, *J. Am. Chem. Soc.*, **108**, 7664 (1986). B. E. Maryanoff and A. B. Reitz, *Phosphorus Sulfur*, **27**, 167 (1986). E. Vedejs and C. F. Marth, *J. Am. Chem. Soc.*, **110**, 3940 (1988). C. Geletneky, F.-H. Försterlin, W. Bock, and S. Berger, *Chem. Ber.*, **126**, 2397 (1993). E. Vedejs and C. F. Marth, *J. Am. Chem. Soc.*, **112**, 3905 (1990). Reviews: M. Schlosser, *Top. Stereochem.*, **5**, 1 (1970). B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89**, 863 (1989). E. Vedejs and M. J. Peterson, *Top. Stereochem.*, **21**, 1 (1994).

[16] S. Wilker, C. Laurent, C. Sarter, C. Puke, and G. Erker, *J. Am. Chem. Soc.*, **117**, 7293 (1995).

[17] U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959). K. Okuma, Y. Yamasaki, T. Komiya, Y. Kodera, and H. Ohta, *Chem. Lett.*,357 (1987). K. Okuma, Y. Tachibana, J. Sakata, T. Komiya, I. Kaneko, Y. Komiya, Y. Yamasaki, S. Yamamoto, and H. Ohta, *Bull. Chem. Soc. Jpn.*, **61**, 4323 (1988). A. P. Krapacho, M. P. Silvon, and S. D. Flanders, *Tetrahe-*

dron Lett., 3817 (1974). E. Vedejs, D. A. Perry, and G. R. Wilde, *J. Am. Chem. Soc.*, **108**, 2985 (1986).

[18] *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis,* edited by L. D. Quin and J. E. Verkade (VCH, New York, 1994).

[19] C. Puke, G. Erker, N. C. Aust, E.-U. Würthwein, and R. Fröhlich, *J. Am. Chem. Soc.*, **120**, 4863 (1998).

[20] I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, and Y. A. Ustynyuk, *Mendeleev Commun.*, 90 (1996).

[21] For a related *stabilized* gauche-betaine type structure derived from ylide addition to CS_2 see: U. Kunze, R. Merkel, and W. Winter, *Chem. Ber.*, **115**, 3653 (1982). E. Schaumann and F.-F. Grabley, *Liebigs Ann. Chem.*, 1702 (1979). H. J. Bestmann, R. Engler, H. Hartung, and K. Roth, *Chem. Ber.*, **112**, 28 (1979).