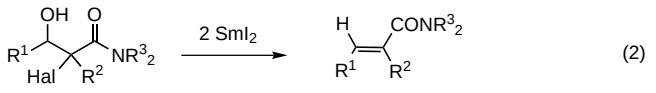

(2)

3a–c **4a–c**

Table 2. Synthesis of α,β-unsaturated amides with SmI_2 [Eq. (2)].

entry	**4**	R^1	R^2	R^3	Hal	*de* [%][a]	yield [%][b]
1	**4a**	C_7H_{15}	H	Et	Cl	> 98	89
2	**4b**	Ph	H	Et	Cl	> 98	90
3	**4c**	MeCH(Ph)	H	Et	Cl	> 98	82

[a] Determined from crude reaction products with GC-MS. [b] Yield of isolated products.

synthesize α,β-unsaturated esters and amides with total *E* stereoselectivity from the easily available 2-halo-3-hydroxy-esters or amides.

Experimental Section

A solution of SmI_2 (1 mmol) in THF (12 mL) was very slowly added dropwise, under a nitrogen atmosphere, to a stirred solution of halohydroxyester **1** (0.4 mmol) in THF (2 mL) at room temperature, until the reaction mixture turned permanently blue. The reaction mixture was quenched with aqueous HCl (1M, 5 mL). Standard work-up and filtration through a pad of Celite provided pure α,β-unsaturated esters **2** (> 98 %).

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[22] The coupling constants between the olefinic protons of compounds **4a**, **4b**, and **4c** were 14.9, 15.3, and 15.2 Hz, respectively, in accordance with the average literature values for J_{trans}.

Investigations of Lipid – Protein Interactions on Monolayers of Chain-Substituted Phosphatidylcholines**

Ursula Dahmen-Levison,* Gerald Brezesinski, Helmuth Möhwald, Jens Jakob, and Peter Nuhn

Polarization-modulated infrared reflection absorption spectroscopy (PM-IRRAS, Figure 1) is a versatile method for studying the hydrolysis of long-chain lipids at the air/water interface and the influence of phase separations on the activity of proteins.[1, 2] Our investigations using this method were performed on phospholipase A_2 (PLA_2). PLA_2 cleaves selectively the *sn*-2 ester linkage of phospholipids, leading to a fatty acid and a lysophospholipid. PLA_2 plays an important role in the arachidonyl cascade, since arachidonyl is the main group found in the 2-position at the glycerol of the phospholipids in mammal cells. PLA_2 is an interfacially active enzyme, whose activity is strongly dependent on the physical-chemical structure of the substrate, which makes it very difficult to develop inhibitors. The investigations at the air/water inter-

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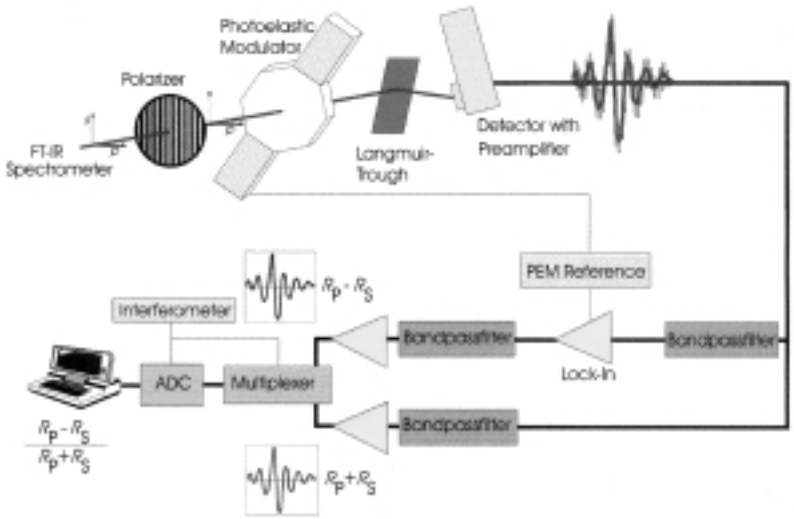


Figure 1. Schematic setup of the PM-IRRA spectrometer.

face have some clear advantages over common techniques. Only very small amounts of phospholipids and enzymes are needed and the physical conditions of the reaction can be varied easily. In many cases phospholipid monolayers with similar thermodynamic and structural parameters can be considered as a single leaflet of a biological bilayer membrane. Especially for interfacial reactions the monolayer offers a reductionistic model.

In an earlier PM-IRRAS study[3] we showed that the enzyme exerts maximal activity in the coexistence region between condensed and liquid-expanded phases. Fluorescence microscopy demonstrated that the enzyme is enriched at the phase boundaries[4] and that this is also the location where the reaction is first detectable.[5] These findings indicate two important features for the PLA_2 activity. First the preorientation of the substrate in the gel phase facilitates the enzyme reaction (Figure 2), and second the reaction can

Figure 2. Model of the preorientation of the substrate induced by enzyme adsorption and of the preferred reaction at defects.

only take place at defects within the membrane. In biological membranes (multicomponent systems) such defects can be created by lipids which are in a condensed state in the vicinity of membrane proteins[6] and by local differences in lipid composition. The turnover rate at high lateral pressures is close to zero.

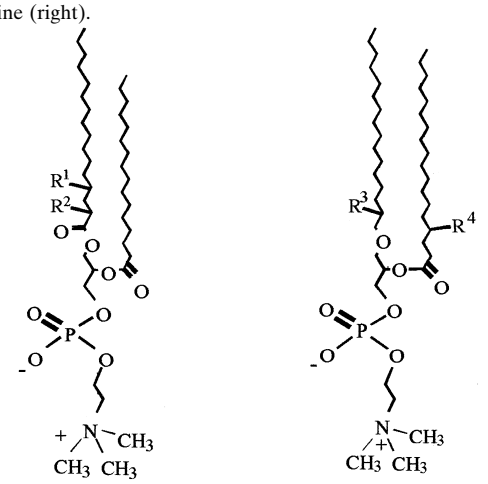
The present investigations were performed with diester and 1-ether-2-ester-glycerophosphocholines (Table 1). The latter were included since they are precursors for plasmalogen and the platelet-activating factor (PAF). Since chain-substituted glycerophosphocholines (PC) have been reported to inhibit the PLA_2 reaction,[7] we introduced lateral branches of various length at different positions into the lipophilic chains.

Monolayers of ether–ester–PC are in general in a more condensed state than those of diester–PC.[8] From the pressure/area diagrams of the chain-substituted PCs the following tendencies were determined:

1) Short-chain branching leads to an increased fluidity in the monolayer. The short chain disturbs the lateral packing of the molecules.[9]
2) A tetradecyl side chain leads to a triple-chain PC. In the compressed state the area per molecule is about 0.62 nm^2. The phase transition pressure (π_c) is shifted to larger values compared to the double-chain analogue.[10]

Figure 3 shows the PM-IRRAS spectrum of a L-DPPC (**1**) monolayer; several characteristic bands can be assigned. The band at 1734 cm^{-1} represents the carbonyl stretching vibration and that at 1469 cm^{-1} the methylene scissoring vibration. Bands at 1230 cm^{-1} and at 1088 cm^{-1} are attributed to antisymmetric and symmetric phosphate stretching vibrations.[11] The phosphate stretching vibrations comprise at least two frequencies. The occurrence of multiple bands indicate the appearance of a heterogenous population of protonated and nonprotonated groups. The broad band at 1159/1170 cm^{-1} and at 1059 cm^{-1} can be assigned to the antisymmetric and symmetric ester stretching vibrations, respectively. Furthermore the band at 971 cm^{-1} is attributed to a vibration of the $C–N^+–C$ group. Carboxylate bands at 1540 and 1581 cm^{-1} with a slight shoulder at 1562 cm^{-1} appear during hydrolysis (Figure 4). They are due to the product (fatty acid) which accumulates in the monolayer during the reaction. In the spectrum of the

Table 1. Diester-glycerophosphocholine (left) ether-ester-glycerophosphocholine (right).



Compd	R^1	R^2	Compd	R^3	R^4
1	H	H	**6**	H	H
2	H	$CH_3(CH_2)_{13}$	**7**	$CH_3(CH_2)_{13}$	H
3	H	CH_3	**8**	CH_3	H
4	CH_3	H	**9**	H	CH_3
5	$CH_3(CH_2)_{13}$	H	**10**	H	$CH_3(CH_2)_{13}$

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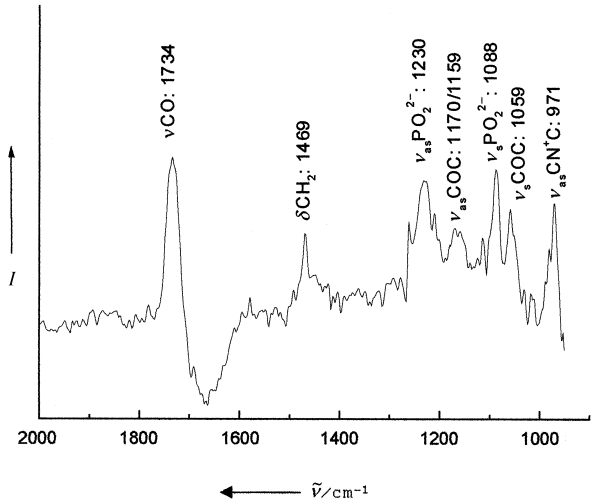

Figure 3. PM-IRRA spectrum of a pure DPPC (**1**) monolayer at a lateral pressure of 40 mN m^{-1}; $T = 20\,^{\circ}$C.

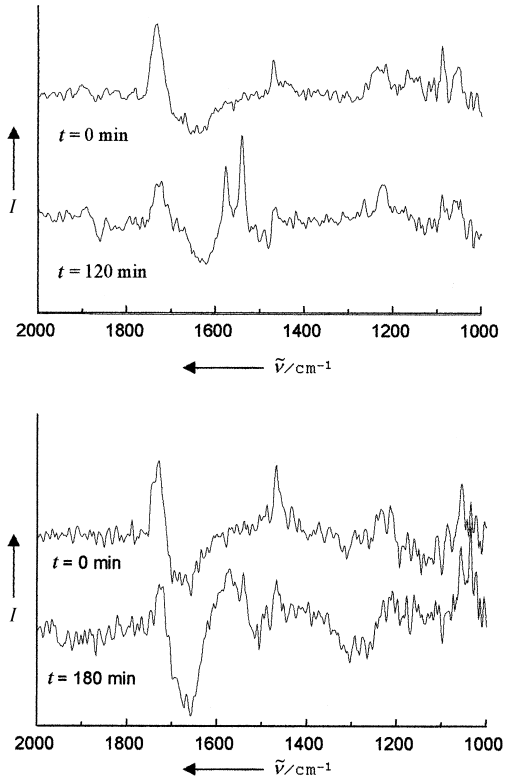

Figure 4. PM-IRRA spectra before ($t = 0$ min) and after a certain reaction time t. Top: **3**, bottom: **5**. $T = 20\,^{\circ}$C, reaction pressure = 8 mN m^{-1}, spectra recorded at 40 mN m^{-1}.

pure fatty acid monolayer one band is observed at 1563 cm^{-1}, which is assigned to the Ca^{2+}-associated carboxy group, and additionally a weak band is observed at 1540 cm^{-1}, which is attributed to a small amount of free carboxylate. The appearance of a band at 1581 cm^{-1} must be caused by an interaction between the protein and fatty acid. The high wavenumber of the band can be explained by a very strong association of the protein with the fatty acid (e.g. partial product inhibition) or by a protein-induced highly condensed state of the calcium carboxylate. In both cases enzyme domains, which build up underneath fatty acid enriched areas, should be responsible for the position of the band. The high intensity of the band at 1540 cm^{-1} can also be explained by a Ca^{2+}-shielding effect of these enzyme domains.

The decrease in intensity of the carbonyl band was used for the quantitative investigation of the hydrolysis reaction. Contrary to the results from Menger et al.,[7] all investigated chain-substituted lipids were catalytically cleaved. The hypotheses that alcylations in the chain region of phospholipids should lead to an inhibitory effect are not supported. From the determined relative hydrolysis rates (see Table 2) the following tendencies are apparent:

1) Phospholipids with unbranched alkyl chains are better hydrolyzed than branched ones.
2) Diester-glycerophosphocholines are cleaved easier than ether-ester-glycerophosphocholines.
3) Methyl-branched phospholipids are hydrolyzed faster than tetradecyl-branched ones.
4) Phospholipids branched at the *sn*-2 chain are cleaved more slowly than those branched at the *sn*-1 chain.

Table 2. Monolayer phase state at 20 °C and 8 mN m^{-1} and yields [%] of the PLA_2-catalyzed hydrolysis after a reaction time t.

Compd	Phase state	t [min]		
		60	120	180
1	con	80	–	–
2	le	ca. 20	–	40
3	con/le	55	70	–
4	le	45	60	–
5	con/le	ca. 20	–	55
6	con	30	–	-
7	con	0	40	85
8	con/le	≤ 10	50	–
9	le	0	0	ca. 20
10	con	0	0	ca. 20

[a] The error in the yield is about 5 to 10% and becomes larger for small reaction rates as well as for the ether – ester and the triple-chain compounds as a result of the smaller intensity; con = condensed, le = liquid-expanded, con/le = two-phase coexistence region.

In analogy to findings for DPPC monolayers, one can assume that also branched PCs have their activity maximum in the two-phase region. Therefore it is important for the present investigation to take the phase properties of each monolayer into consideration. At the chosen reaction pressure (8 mN m^{-1}) the compounds investigated are in different phase states (see Table 2). The increase in reactivity of **3** compared to **4** and of **2** compared to **5** could be explained considering their phase properties. Further investigations performed at the same reduced pressure (π/π_c) are necessary before final conclusions can be drawn about the influence of the substitution position (2 or 4) on the reaction rates.

Experimental Section

L-Dipalmitoylphosphatidylcholine (L-DPPC, **1**) was purchased from Sigma (Taufkirchen, Germany). Diester-glycerophosphocholines were synthesized from 2,5-di-*O*-benzyl-D-mannitol. In the final reaction steps, 2-*O*-benzyl-*sn*-glycerophosphocholine was acylated with the desired branched acid anhydride. The benzylic group was subsequently removed from the 1-acyl-2-*O*-benzyl-*sn*-glycerophosphocholines which were then acylated with stearic acid anhydride to form **2**–**5** (recovered yields between 60–

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75%). The 1-ether-2-ester-glycerophosphocholines (**6**–**10**) were synthesized starting with *R*-(−)-1,2-isopropylideneglycerol. The obtained 1-*O*-alkyl-2-*O*-benzyl-*sn*-glycerophosphocholines were in the last step debenzylated and immediately acylated with the desired acid anhydride (recovered yields between 60–75%). Purification was performed by column chromatography.

2: $C_{56}H_{112}NO_8P$ (M_r = 958.48); calcd: P 3.23; found: P 3.40; ES-MS (*m*/*z*): 959.1 [*M*+H$^+$], 981.0 [*M*+Na$^+$]. **3**: $C_{43}H_{86}NO_8P$ (M_r = 776.13); calcd: P 3.99; found: P 4.15; ES-MS (*m*/*z*): 777.9 [*M*+H$^+$], 799.6 [*M*+Na$^+$], 815.9 [*M*+K$^+$], 1552.3 [2*M*+H$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.51 (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.79 (s, 2H; NCH_2), 4.10 (m, 2H; glycerol-*sn*-3-CH_2), 5.00 (m, 1H, glycerol-*sn*-2-CH). **4**: $C_{45}H_{90}NO_8P$ (M_r = 804.18); calcd: P 3.85; found: P 3.71; ES-MS (*m*/*z*): 805.6 [*M*+H$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.5 (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.80 (s, 2H; NCH_2), 4.02 (m, 2H; glycerol-*sn*-3-CH_2), 5.03 (m, 1H; glycerol-*sn*-2-CH). **5**: $C_{58}H_{116}NO_8P$ (M_r = 986.53); calcd: P 3.14; found: P 3.29; ES-MS (*m*/*z*): 987.5 [*M*+H$^+$], 1010.4 [*M*+Na$^+$], 1026.6 [*M*+K$^+$]. **6**: $C_{42}H_{86}NO_7P$ (M_r = 748.12); calcd: P 4.14; found: P 4.02); ES-MS (*m*/*z*): 749.5 [*M*+H$^+$], 771.3 [*M*+Na$^+$], 787.3 [*M*+K$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.6 (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.80 (s, 2H; NCH_2), 4.02 (m, 2H; glycerol-*sn*-3-CH_2), 5.07 (m, 1H; glycerol-*sn*-2-CH). **7**: $C_{56}H_{114}NO_7P$ (M_r = 944.49); calcd: P 3.28; found: 3.21; ES-MS (*m*/*z*): 945.4 [*M*+H$^+$], 967.4 [*M*+Na$^+$], 983.3 [*M*+K$^+$]. **8**: $C_{43}H_{88}NO_7P$ (M_r = 762.14); calcd: P 4.06; found: 3.99; ES-MS (*m*/*z*): 763.0 [*M*+H$^+$], 785.0 [*M*+Na$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.6 (m, 2H; glycerol-*sn*-1-CH_2), 4.05 (m, 1H; OCH_2CH), 4.15 (m, 2H; glycerol-*sn*-3-CH_2), 4.55 (s, 2H; CH_2CH_2N), 5.05 (m, 1H; glycerol-*sn*-2-CH). **9**: $C_{43}H_{88}NO_7P$ (762.24); calcd: P 4.06; found: 3.99); ES-MS (*m*/*z*): 763.3 [*M*+H$^+$], 1525.2 [2*M*+H$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.6 (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.80 (s, 2H; NCH_2), 4.1 (m, 2H; glycerol-*sn*-3-CH_2), 4.54 (s, 2H; CH_2CH_2N), 5.10 (m, 1H; glycerol-*sn*-2 CH). **10**: $C_{56}H_{114}NO_7P$ (944.49); calcd: P 3.28; found: 3.35; ES-MS (*m*/*z*): 945.2 [*M*+H$^+$], 967.2 [*M*+Na$^+$], 983.0 [*M*+K$^+$].

Monolayer experiments: A buffer of NaCl (150 mM), $CaCl_2$ (5 mM), and Tris (10 mM) at a pH of 8.9 was utilized as the subphase. The film balance (R&K ,Wiesbaden, Germany) was equipped with an Wilhelmy-type pressure measuring system. Phospholipase A_2 of the venom from *Crotalus Atrox* was used for hydrolysis (660 units per mg protein, Sigma, Germany). The enzyme was dissolved in buffer, at 40 mN m^{-1} injected underneath the monolayer (6 ng protein per mL subphase) and carefully stirred. The hydrolysis was monitored at a constant lateral pressure of 8 mN m^{-1}. After 60, 120, or 180 min the monolayer was compressed to 40 mN m^{-1} and a spectrum was recorded. All experiments were performed at 20 °C.

PM-IRRAS experiments: The IR beam was decoupled from a Bruker IFS66 spectrometer (Bruker, Karlsruhe, Germany), linearly polarized (KRS5, Specac, Orpington, UK) and passed through a photoelastic modulator (ZnSe, Type II, Hinds). The beam was then reflected from the water surface and focused with a ZnSe lense on the nitrogen-cooled MCT detector (Figure 1). With the polarization modulation one can nearly fully delete the influence of isotropic water absorption since the parallel (R_p) and the normal (R_s) to the plane of incidence polarized reflectivity was determined simultaneously. With the electronic setup one can obtain (bandpassfilter: 300–1200 Hz, Stanford Research System, model SR 650; EG&G lock-in amplifier, model 5209) the differential signal $(R_p - R_s)/(R_p + R_s)$, with a contribution from only the anisotropic absorption of the monolayer.

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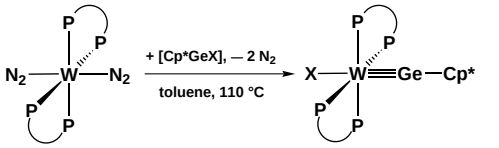
Synthesis and Structure of the Germylyne Complexes *trans*-[X(dppe)$_2$W≡Ge(η^1-Cp*)] (X = Cl, Br, I) and Comparison of the W≡E Bonds (E = C, Ge) by Density Functional Calculations **

Alexander C. Filippou,* Athanassios I. Philippopoulos, Peter Portius, and Dirk U. Neumann

A large number of transition metal carbyne complexes have been described and their reactions investigated in depth.[1] However, complexes containing a triple bond between a transition metal and a heavier element of the fourth main group (E = Si, Ge, Sn, Pb) are very rare. To the best of our knowledge silylyne,[2] stannylyne and plumbylyne complexes are unknown, and for germylyne complexes there are only the compounds [(η^5-C_5H_5)(CO)$_2$M≡GeR] (M = Cr, Mo, W) containing a sterically very demanding substituent R (R = 2,6-$Trip_2C_6H_3$, 2,6-$Mes_2C_6H_3$; Trip = 2,4,6-*i*$Pr_3C_6H_2$; Mes = 2,4,6-$Me_3C_6H_2$).[3] Here we report a new route to germylyne complexes carrying a pentamethylcyclopentadienyl group on the germanium atom. Our route exploits the thermal elimination of N_2 from *trans*-[W(dppe)$_2$(N_2)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) (**1**).[4]

The reaction of **1** with the germylenes [Cp*GeX] **2a**–**c** (X = Cl, Br, I)[5] in boiling toluene leads smoothly to the germylyne complexes **3a**–**c**, respectively [Eq. (a)]. The complexes **3a**–**c** which each contain one equivalent of



1 **3a-c**

X = Cl, Br, I; P⌒P = dppe; Cp* = C_5Me_5

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