Dialkylamidoderivatives of Sn(II) and Sn(IV) in Phosphorus Chemistry

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Abstract

Dialkylamido derivatives of tin, $Sn(NR_2)_2$ and $Sn(NR_2)_4$ react with dialkyl phosphites $(RO)_2P(O)H$ with displacement of one or two ester functions at phosphorus by the dialkylamino groups. ^{31}P NMR spectroscopy indicates the formation of P^V intermediates, whereas ^{119}Sn NMR spectroscopy suggests that the reactivity of organophosphorus substrates is (at least partially) determined by the initial Lewis acid–base complexation with the Sn reagent.

Introduction

In previous communications [1, 2] we reported that titanium tetrakis(diethylamide), $Ti(NEt_2)_4$ (1), is capable of displacing both ester functions in the diesters of phosphorus acid, $(RO)_2P(O)H$ (2), and is unreactive towards phosphate triesters, $(RO)_3PO$ (3). The manganese diethylamide $Mn(NEt_2)_2$ (4), on the other hand, replaced one ester function in 3, and one or both in 2. Compounds 1 and 4 were chosen for those studies due to their reported [3] reactivity towards aldehydes and ketones and their use as chemoselective protecting reagents. Because of the complex pattern of the chemical reactivity of 1 and 4 towards organophosphorus substrates, and because we have recently shown [4] that Sn(II) and Sn(IV) dialkylamidoderivatives react in the anchimerically assisted process with α-hydroxyphosphonic diesters, we decided to include into our studies the investigation of the reactivity of the compounds containing the $Sn-NR_2$ function with esters of phosphorus oxyacids. Lewis acid reactivity of $SnCl_4$ has been used [5] in the chelation controlled reactions of carbonyl compounds, and this reagent is known [6] to form a donor–acceptor complex with ethyl ethylphosphinate. Tributylaminostannanes, (Bu_3SnNR_2), have been found [7] to react with carbonyl substrates in two different ways, depending on the steric requirements of the R groups, and showed some similarities to the reactions of ketones with titanium(IV) reagents [8]. In view of the rich and diverse reactivity of tin–nitrogen compounds [9] and of the reactivity of the tin atom towards the phosphoryl oxygen atom, we hoped that reactions between Sn(II) and Sn(IV) amides and organophosphorus esters would provide us with more information about the exchange processes at the phosphorus atom.

Results and Discussion

Sn(II) Derivatives

Bis(dialkylamido) tin(II) compounds, $Sn(NR_2)_2$ (5), were prepared from $SnCl_2$, R_2NH, and BuLi by the procedures reported in the literature [10]. In full analogy to the titanium reagent (1) [1], bis(diethylamido) tin (**5a**, 5, R = Et) was found to be totally unreactive towards triethyl phosphite, $(EtO)_3P$, triethyl phosphate, $(EtO)_3PO$, as well as diethyl benzylphosphonate, $PhCH_2P(O)(OEt)_2$. With respect to triethyl phosphate, **5a** shows therefore much lower reactivity than its manganese analogue (4), which displaces one EtO group yielding diethyl *N,N*-diethylphosphoroamidate, $(EtO)_2P(O)NEt_2$ [2]. **5a** reacted, however, with dialkyl phosphites; after 3 h at room temperature, dimethyl phosphite (**2a**, 2, R = Me) was completely converted to bis(diethylamido)phosphorus acid (**6a**).

$$\underset{\mathbf{2a}}{(MeO)_2P(O)H} + \underset{\mathbf{5a}}{(Et_2N)_2Sn} \longrightarrow \underset{\mathbf{6a}}{(Et_2N)_2P(O)H} \quad (1)$$

With respect to substrates 2, tin reagent **5a** is, however, less reactive than the titanium analogue **1**; when reaction (1) was interrupted after 0.5 h unreacted **2a** was still present in the reaction mixture, whereas when treated with **1**, **2a** is fully converted to **6a** within less than 0.5 h [1].

Reaction between **5a** and diethyl phosphite (**2b**, 2, R = Et) yielded, depending on the conditions, the products of substitution of one, or both, EtO groups by the Et_2N substituent.

$$\underset{\mathbf{2b}}{(EtO)_2P(O)H} \xrightarrow{\mathbf{5a}} \underset{\mathbf{7a}}{(EtO)(Et_2N)P(O)H} + \mathbf{6a} \quad (2)$$

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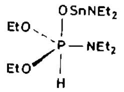
The attempts to optimise reaction (2) were made by changing the reaction time (1–3 h), temperature (25–40 °C), and the initial molar ratio **5a**/**2b** (0.5–2). When **2b** was treated with diethylamine in the presence of $SnCl_2$ alone, no reaction took place; thus $SnCl_2$ does not act as a catalyst, but the covalent tin–nitrogen compound **5a** is necessary for the substitution of the EtO by Et_2N groups. Under no conditions was **7a** the dominant component of the product; lower temperature and lower **5a**/**2b** ratios resulted in low conversions, with up to 40% of unreacted **2b** present in the reaction product. At higher temperatures and higher values of **5a**/**2b** the disubstitution was a major reaction, and when reaction (2) was carried out at 40 °C for 3 h, with **5a**/**2b** = 2, no **2b** was present in the reaction product which consisted almost exclusively of the disubstitution product **6a**. Reaction (2) is therefore not selective enough to serve as a general route to mixed phosphorus amidoesters **7**. The lower reactivity observed for **2b** as compared with **2a** results almost certainly* from the greater steric hindrance of the EtO groups (as compared with two MeO groups). As in the case of the reaction with **2a**, reagent **5a** is less reactive than the titanium compound **1** with respect to phosphite **2b**. When reacting **2b** and **5a** in a 1:1 ratio at 40 °C for 2 h the unreacted phosphite, mono- and disubstituted products are formed in a 0.5:4:5.5 ratio. This result shows that more than half (*c.* 75%) of the diethylamino groups initially present in **5a** have been transferred from tin to phosphorus, so that one molecule of **5a** is capable of transferring *both* NEt_2 groups to a phosphoryl centre.

Steric effects on the functional groups exchange between tin and phosphorus can be also demonstrated by changing the bulk of substituents R in reagent **5**. When **2b** was treated with bis(di-n-butylamido)tin (**5b**, **5**, R = n-Bu) only the monosubstituted product **7b** was formed, irrespective of the excess of **5b** or reaction temperature.

$$\underset{}{\mathbf{2b}} + \underset{\mathbf{5b}}{(n\text{-}Bu_2N)_2Sn} \longrightarrow \underset{\mathbf{7b}}{(EtO)(n\text{-}Bu_2N)P(O)H} \qquad (3)$$

In order to gain more insight into the mechanism of the amination, reaction (2) was monitored by means of ^{31}P NMR spectroscopy. The hexadeuteriobenzene solutions of the reaction mixture of **2b** and **5a** were incubated at 40 °C and the ^{31}P NMR spectra of these solutions were recorded periodically. With the initial ratio **5a**/**2b** = 1 the first change in the ^{31}P NMR spectrum observed was a formation of the broad peak at −51.8 ppm (−49.7 ppm relative to 85% H_3PO_4), in addition to the signal of **2b** at 5.0 ppm. This new signal has been assigned to a P^V intermediate **8a** formed by the addition of the Et_2N–$SnNEt_2$ system to the phosphoryl group in **2b**.

2b + **5a** ⟶



(4)

8a

It has been reported [12] that covalent derivatives of pentacoordinated phosphorus, containing two P–O, one P–N, one P–H and one P–Ar bonds show in their ^{31}P NMR spectra signals in the range −45 to −50 ppm (relative to 85% H_3PO_4). Intermediate **8a** will be expected to collapse by a transfer of the EtO group from phosphorus to tin, with the formation of the phosphorus monoamide **7a**. This product is observed after 7 min, yielding a signal at 10.9 ppm, at the expense of the substrate's signal at 5.0 ppm.

$$\mathbf{8a} \longrightarrow \mathbf{7a} + \underset{\mathbf{5c}}{Sn(OEt)(NEt_2)} \qquad (5)$$

After 30 min the subsequent formation of the disubstitution product **6a** (δ 17 ppm) can be observed. The results of this experiment are presented in Fig. 1.

With an excess of **5a** (**5a**/**2b** = 2) the reaction is faster and after 30 min the ^{31}P NMR spectrum revealed the presence of **6a** as a major product, some **7a**, as well as two high-field signals (δ −48.5, −51.8 ppm), most likely corresponding to the P^V intermediates of the first and second substitution steps. It is proposed therefore that the amination of dialkyl phosphites (**2**) by bis(dialkylamido)tin (**5**) involves a sequence of additions to the phosphoryl group, followed by the exchange of functional groups between phosphorus and tin atoms.

Sn(IV) Derivatives

Tetrakisdiethylamido tin(IV), $Sn(NEt_2)_4$ (**9**), was prepared according to the literature procedure [13]. Similar to its Ti(IV) analogue [1], as well as to **5a**, this reagent showed no sign of reactivity towards triethyl phosphite or phosphate, and diethyl benzylphosphonate. Reaction with diethyl phosphite (**2b**), however, resulted in the exchange and yielded mixtures of the mono- and diaminated products, **7a** and **6a**. The observed rigorous selectivity with respect to dialkyl phosphites (**2**) and other tetracoordinate phosphoryl substrates can originate at the level of the initial Lewis acid–base complexation between phosphorus and tin compounds, or at the level of the actual exchange of the functional groups. To test whether the exchange reaction is determined by the ability of a tin reagent to form

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*We have recently observed [11] that steric bulk of substituents of phosphorus plays an essential role in the rate of the titanium(IV)-mediated exchange of functional groups at phosphorus atom.

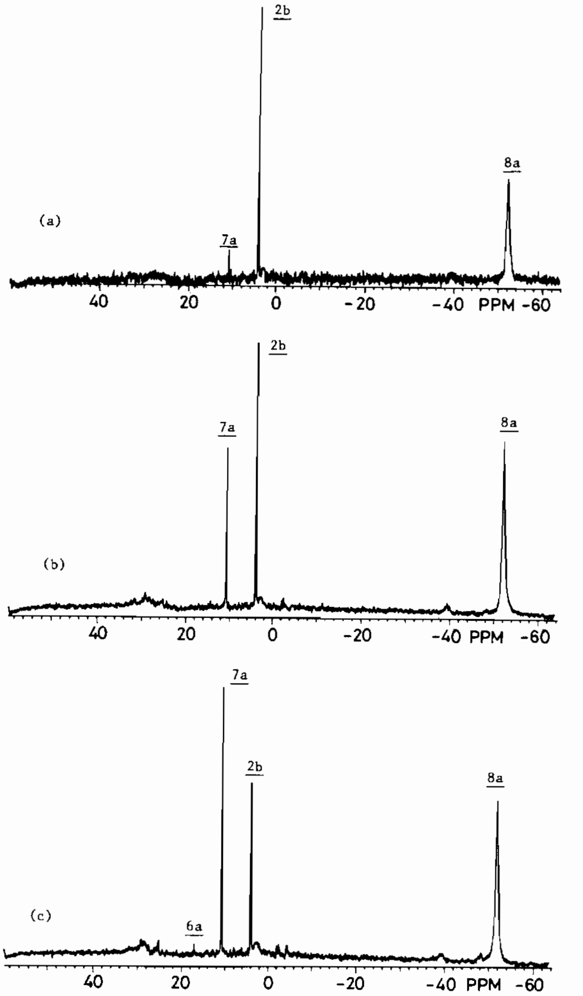

Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of the equimolar mixture of **2b** and **5a** in C_6D_6, 40 °C: (a), 2 min; (b), 7 min; (c), 30 min.

a donor–acceptor complex with a given organophosphorus substrate, we have carried out some experiments involving ^{119}Sn NMR spectroscopy. The 2:1 complexation of trimethyl phosphate by $SnCl_4$ is well known and has been studied by ^{1}H and ^{31}P NMR spectroscopy [14]. It was reported [14] that such complexation leads to significant broadening of the ^{119}Sn signal in the ^{119}Sn NMR spectrum of the reaction mixture. We have found that upon the addition of two mole equivalents of trimethyl (as well as triethyl) phosphate to the solution of $SnCl_4$ in C_6D_6, the original broad signal of the ^{119}Sn nuclei (δ −150.0) disappeared completely, and no new signals were observed. We conclude therefore that phosphates $(RO)_3PO$ bond strongly to $SnCl_4$, causing further broadening of the ^{119}Sn signal, probably due to the ^{31}P–^{119}Sn spin–spin coupling. When two mole equivalents of triethyl phosphate were added to the solution of **9** in C_6D_6 (a system for which *no reaction* was observed), the ^{119}Sn NMR spectrum of the initial solution remained unchanged, with the ^{119}Sn signal (δ −120.0) not markedly broadened. However when two mole equivalents of **2b** were added to the solution of **9** (a system which *does* lead to the exchange), the ^{119}Sn signal at −120.0 ppm disappeared completely from the spectrum. It seems therefore that phosphoryl substrates, such as dialkyl phosphites, phosphates or phosphonates, differ greatly (possibly for steric reasons) with respect to their ability to interact with such weak Lewis acids as **9**; these interactions being in turn a necessary condition for the subsequent exchange of functional groups between tin and phosphorus.

Unlike the case of the reaction between **2b** and **5a** (reaction 2), increase of reaction temperature or duration, as well as increase in the initial **9**/**2b** ratio, never resulted in the full conversion of **2b** into **6a**. The results obtained for the reaction of **2b** with **9** under various conditions are summarized in Table 1. It can be clearly seen that after the initial ratio of unity for **9**/**2b** is reached, neither the further increase of this ratio, nor the increase of the reaction time (last seven entries in Table 1) affects significantly the products ratio, **6a**/**7a**, which remains approximately constant (2.30 ± 0.26). This result was supported by the ^{31}P NMR spectroscopic examination of the **9** + **2b** reaction mixture in a 1:1 molar ratio. The signals corresponding to the mono- (**7a**) and disubstituted (**6a**) products (δ 10.8 and 17.0 ppm, respectively) appeared very soon in the spectrum, while the relative intensity of these signals (and that of unreacted **2b**) did not significantly change with time. Similarly, the ^{1}H NMR spectroscopy demonstrated fast formation of products containing P–NCH_2 (δ *c.* 2.8 ppm) and $SnOCH_2$ [10b] (δ c. 3.5 ppm) functional groups. The most likely explanation for this behaviour can be based on the assumption that the reaction products **7a** and **6a**, representing the first and the second NEt_2 group transfer from Sn(IV) to P, achieve fast equilibrium. In such case, the ratio **6a**/**7a** would be expected to remain constant irrespective of the initial **9**/**2b** ratio.

Fast ligand exchange between Sn(IV) atoms has been documented for SnX_4 (X = Cl, Br, I) species [15]. We have measured the ^{1}H decoupled ^{119}Sn NMR spectra for the variable concentrations (0.8–3.2 M) of **9** in C_6D_6 and found no significant effect of the concentration of **9** on the ^{119}Sn chemical shift value (−120 ppm). The NMR signal was however in all cases very broad (*c.* 45 Hz at half-height), and showed the fine structure indicative [15] of the fast exchange of the substituents. It seems therefore that the mixture of **2b** and **9** represents a dynamic system involving fast exchange of amino and alkoxy groups between the two (Sn and P) centers.

TABLE 1. The reaction between **2b** and **9** (n-hexane, 40 °C)

Molar ratio (**9**/**2b**)	Reaction time (h)	Molar ratio (products)[a]		
		unreacted **2b**	**7a**	**6a**
0.05	24	9.6	0.4	0.0
0.08	24	8.9	1.1	0.0
0.25	24	4.0	5.5	0.5
0.50	24	3.6	4.0	2.4
1.00	24	1.5	2.9	5.6
2.00	24	0.4	3.2	6.4
2.50	24	0.4	3.0	6.6
3.00	24	0.3	2.8	6.9
4.00	24	0.3	2.7	7.0
2.00	48	0.6	2.8	6.6
2.00	120	0.8	2.6	6.6

[a]The ratios of three organophosphorus compounds (**2b**, **7a**, **6a**) were determined from the integrated peak areas for the P–H signals in the ^{1}H NMR spectra of reaction products.

$$\mathbf{2b} + \underset{\mathbf{9}}{\mathrm{Sn(NEt_2)}_n\mathrm{(OEt)}_{4-n}} \rightleftharpoons \mathbf{7a} + \underset{\mathbf{9a}}{\mathrm{Sn(NEt_2)}_{n-1}\mathrm{(OEt)}_{5-n}} \qquad (6a)$$

$$\mathbf{7a} + \mathbf{9}\ (\mathbf{9a}, \text{etc}) \rightleftharpoons \mathbf{6a} + \mathbf{9a}\ (\text{etc}) \qquad (6b)$$

$n = 1, 2, 3, 4$

In conclusion, amidoderivatives of Sn(IV) are less reactive in the ester–amide group exchange at phosphorus than the Sn(II) analogues (**5**), which, in turn, have been found to be less reactive than the Ti(IV) compounds (**1**). With respect to the organophosphorus substrates studied, the qualitative requirements of all three reagents are similar: it has to contain the phosphoryl group, and one of the groups at the phosphorus centre must be (probably for steric reasons [11]) the hydrogen atom. Further aspects of the ester–amide group exchange at phosphorus are being investigated in our laboratories.

Experimental

NMR spectra were recorded on a superconducting FT Bruker AC 300 spectrometer with TMS (^{1}H, ^{13}C) as internal standard, and trimethyl phosphate (^{31}P) and tetramethyltin (^{119}Sn) as external standards. Mass spectra were recorded on a VG Micromass 16F spectrometer. IR spectra were recorded on a Beckman 4250 spectrophotometer. Elemental analysis were performed at the University of Cape Town using a Heraeus Universal combustion analyser.

All reactions using reagents **5** were carried out *in situ*, in dry n-hexane, in an atmosphere of dry nitrogen. Reagent **9** was distilled immediately before use and reacted in dry benzene under N_2. Organophosphorus substrates were either commercially available, or prepared according to standard procedures. All reagents and substrates were dried and purified in the conventional manner.

Preparation of Reagents 5

5a was prepared as described in the literature [10]. An aliquot of the freshly prepared solution of **5a** in n-hexane (pale yellow clear solution with some precipitate of LiCl) gave a black solution on addition of aq. $AgNO_3$ indicating the presence of divalent tin. The aliquot was also examined by ^{1}H NMR spectroscopy (C_6D_6) and revealed, in addition to the signals of n-hexane, the following signals: δ 1.07 (12H, t, J_{HH} 7.0 Hz, 4 × CH_3 of Et); 3.07 (8H, q, J_{HH} 7.0 Hz, 4 × CH_2 of Et). Literature data [10b]: δ 1.13; 3.20, respectively.

5b was prepared in the same manner as **5a**, and the freshly prepared solutions of reagents **5** were used immediately for further reactions.

Reactions of 5 with Organophosphorus Substrates

The substrate was syringed into the clear yellow solution of **5** in n-hexane and the mixture was stirred at 25 or 40 °C for the required period of time with the exclusion of moisture. Ethanol, and next water, were added. The mixture was extracted with CH_2Cl_2, the organic layer was dried ($MgSO_4$), and the solvent and other volatile products were evaporated under reduced pressure. The NMR spectra of the crude product were recorded and the individual products were identified by comparing these spectra with those of the authentic samples, prepared by alternative methods [1, 16]. The phosphoroamidites (**7**) and diamidites (**6**) were not purified by distillation, due to their known [17] thermal instability.

Reaction between 5a and 2a

This reaction (1:1, 25 °C, 3 h) afforded bis(diethylamido) phosphorus acid (**6a**); yield 45%. ^{1}H NMR ($CDCl_3$): δ 1.10 (12H, t, J_{HH} 7.2 Hz, 4 × CH_3); 3.06 (8H, d of q, J_{HH} 7.2 Hz, J_{HP} 11.9 Hz, 4 × CH_2); 6.72 (1H, d, J_{HP} 569.3 Hz, P–H). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 17.16. MS (EI): m/z 192 (M^+, 40%). IR: 2360 cm^{-1} (ν_{PH}). The data obtained for this product were identical to those obtained previously for **6a** [1].

Reactions between 5a and 2b

These reactions afforded, depending on reaction conditions, variable proportions of unreacted **2b**, **7a** and **6a**. **2b** and **6a** were identified by comparison with authentic samples. **7a** was identified according to the following spectroscopic evidence. ^{1}H NMR ($CDCl_3$): δ 1.14–1.54 (9H, m, 2 × CH_3, CH_3); 2.92 (4H, d of q, J_{HH} 7.0 Hz, J_{HP} 12.8 Hz, 2 × NCH_2);

3.90 (2H, d of q, J_{HH} 7.0 Hz, J_{HP} 8.1 Hz, OCH_2); 6.78 (1H, d, J_{HP} 622.0 Hz, P–H). ^{31}P NMR (coupled, $CDCl_3$): δ 11.5 (d of t of quint, J_{PH} 622.0 Hz, J_{POCH} 8.2 Hz, J_{PNCH} 12.8 Hz). MS (EI): m/z 166 ($(M + 1)^+$ 40%); 165 (M^+, 10%); 150 ($(M - CH_3)^+$, 10%); 72 (Et_2N^+, 30%). IR: 2362 cm^{-1} (ν_{PH}). Spectroscopic data of this product were identical to those obtained for 7a prepared independently from diethylamine and the ethyl phosphorus acid anhydride, (EtO)HP(O)–O–P(O)H(OEt) [16a], and from Et-OPO_2H_2, diethylamine, Ph_3P, and CCl_4 [16b].

Under the conditions of 5a/2b = 2, 40 °C, 3 h, **6a** (47%) was the exclusive reaction product.

Reactions between 5a and 2b; ^{31}P NMR studies

A solution of **5a** in n-hexane (0.8 ml) was transferred to an NMR tube, 0.2 ml of benzene-d_6 was added and the solution was kept in a water bath at 40 °C. The required quantity (0.30–0.65 mmol) of **2b** was syringed into the solution, the ^{31}P NMR of this solution was recorded immediately, and then the spectra were recorded again at the required time intervals.

Reactions between 5b and 2b

The reactions were carried out using the molar ratio **5b**/**2b** = 1, at 25 °C for 3 h, and **5b**/**2b** = 2, at 40 °C for 3 h. In both cases ethyl *N,N*-dibutylphosphoroamidite (**7b**) was formed in 45% yield, and was identified by comparing its spectroscopic properties with those obtained for this compound prepared from dibutylamine and ethylphosphorus acid anhydride [16a]. ^{1}H NMR ($CDCl_3$): δ 0.92 (6H, t, J_{HH} 7.0 Hz, $2 \times CH_3$); 1.11–1.99 (11H, m, $4 \times CH_2$, CH_3); 2.77 (4H, b.t, J_{HH} 7.0 Hz, $2 \times NCH_2$); 3.87 (2H, d of q, J_{HH} 7.0 Hz, J_{HP} 8.1 Hz, OCH_2); 6.78 (1H, d, J_{HP} 609.4 Hz, P–H). ^{31}P NMR (coupled, $CDCl_3$): 10.1 (d of t, J_{PH} 610.4 Hz, J_{POCH} 8.2 Hz). MS (EI): m/z 222 ($(M + 1)^+$, 10%); 221 (M^+, 10%); 178 ($(M - Pr)^+$, 5%); 128 (Bu_2N^+, 5%). IR: 2343 (ν_{PH}).

Preparation of 9

This reagent was prepared from $SnCl_4$, diethylamine and BuLi according to the procedure given in the literature [13]. Yield 73%; boiling point, 110 °C (0.5 mm); yellow–red liquid (yellow in benzene). ^{1}H NMR (CCl_4): δ 1.04 (24H, t, J_{HH} 7.1 Hz, $8 \times CH_3$); 3.00 (16H, q with $Sn^{117,119}$ satellites, J_{HH} 7.1 Hz, $J_{HSn^{117,119}}$ 49.84 Hz; the satellites are split into doublets by Sn^{117} and Sn^{119}, $8 \times CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, TMS): δ 16.77(CH_3); 44.34(CH_2). *Anal.* Calc. for $C_{16}H_{40}N_4Sn$: C, 47.2; H, 9.8; N, 13.8. Found: C, 48.0; H, 9.5; N, 13.4%. The spectra of **9** agreed well with the data given for this compound in the literature [13, 18].

Reactions of 9 with Organophosphorus Substrates

9 was dissolved in benzene and the required amount of substrate was syringed into this solution under nitrogen. After incubating the reaction mixture at required temperature and for the required period of time, ethanol, followed by water was added, the mixture extracted with CH_2Cl_2, the organic layer dried ($MgSO_4$), and volatile components were removed under reduced pressure. The crude reaction products were examined and identified spectroscopically, as described before.

Acknowledgements

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