$R1 = 0.0945$ for 4546 data with $F > 4\sigma(F)$; $wR2 = 0.2583$, GOF = 0.96 for all 10707 data (F^2); 571 parameters; Flack $x = 0.07(3)$. All copper, acetonitrile, and PF_6^- atoms were anisotropic except the fluorine atoms on the disordered PF_6^- ion.

X-ray data were collected at 168 K for **1** and 173 K for **2** on a Bruker SMART diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Reflections were collected in the range $4 < 2\theta < 53°$, and a semiempirical absorption correction was applied. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137503 and -137504. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Intermolecular Trapping of the Nazarov Intermediate: Domino Electrocyclization/[3+2] Cycloadditions with Allylsilanes[**]

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Reactions that entail the stereoselective creation of multiple carbon–carbon bonds are highly valued for their synthetic utility.[1] In particular, one-step processes that convert readily available, acyclic components into fused or bridged polycyclic products offer a powerful method for increasing molecular complexity.[2] We have described several examples of the deliberate intramolecular trapping of oxyallyl cations generated during the Nazarov cyclization[3] of 1,4-dien-3-ones, which has resulted in the high yield and stereoselective formation of diverse polycyclic products.[4] These studies were predicated on the idea that a pendant alkene trap could intercept the oxyallyl cation intermediate at a rate competitive with the normal elimination pathway, a process that we have termed the "interupted Nazarov" reaction. More surprising was our observation of the high-yield intermolecular trapping of the Nazarov intermediate using silyl hydride.[5] This occurrence suggests a much broader potential for this process.

These results prompted us to investigate the use of simple allylic silanes in the intermolecular trapping of Nazarov intermediates.[6] The well-precedented nucleophilic reactivity of allylsilanes[7] and their relative stability under Lewis acidic conditions suggested that they might function as effective traps of the oxyallyl cation intermediate. The expected 2-allylcyclopentanones could serve as useful building blocks in the construction of a variety of cyclopentanoid targets. Surprisingly, simple allylation was found to be a minor pathway—the major products in most cases were unprecedented bicyclo[2.2.1]heptanones resulting from a formal [3+2] addition of the oxyallyl cation and the alkene.[8, 9] Described below are the preliminary results of this study, which offers a novel, one-step preparation of bridged bicyclic systems from two simple, unsaturated fragments.

Initial experiments employed dienone **1a**[10a,b] and allyltrimethylsilane (**2a**). Treatment of a mixture of these two compounds with $BF_3 \cdot OEt_2$ at low temperature resulted in the formation of several diastereomeric allylated cyclopentanones (**3a–c**) in a combined yield of 43%, along with 49% of an entirely different product (as a single isomer) lacking any unsaturation (Scheme 1). The presence of a trimethylsilyl group suggested that this product was either bicyclo[2.2.1]heptanone **4a** or the isomeric bicyclo[3.2.1]octanone **5**, which result from either direct ring closure of the intermediate

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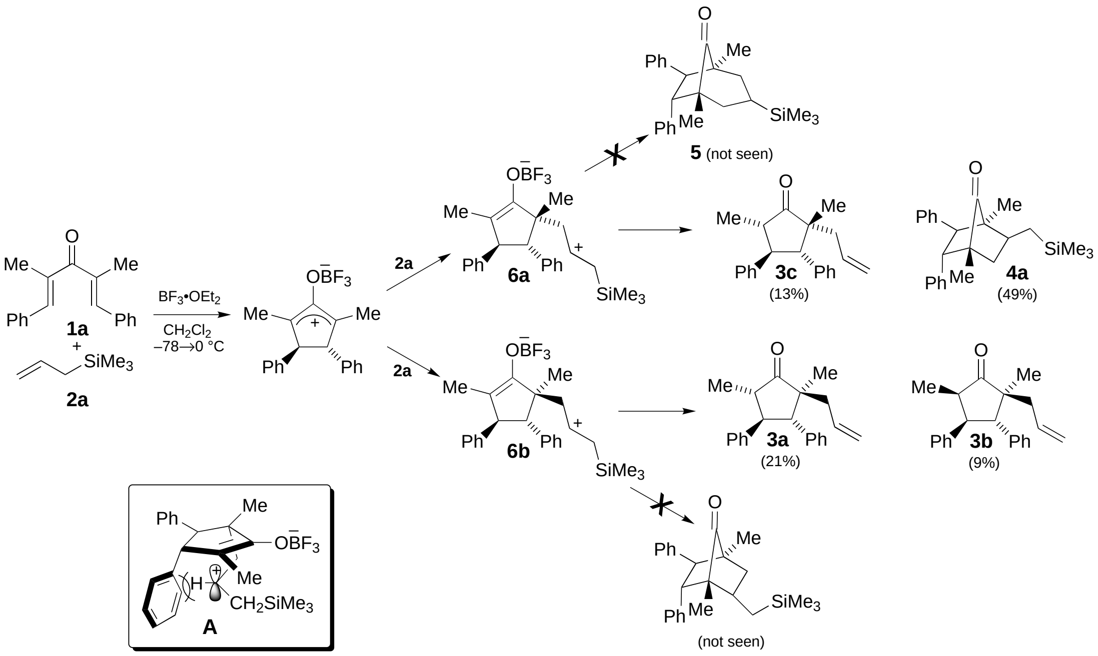


Scheme 1.

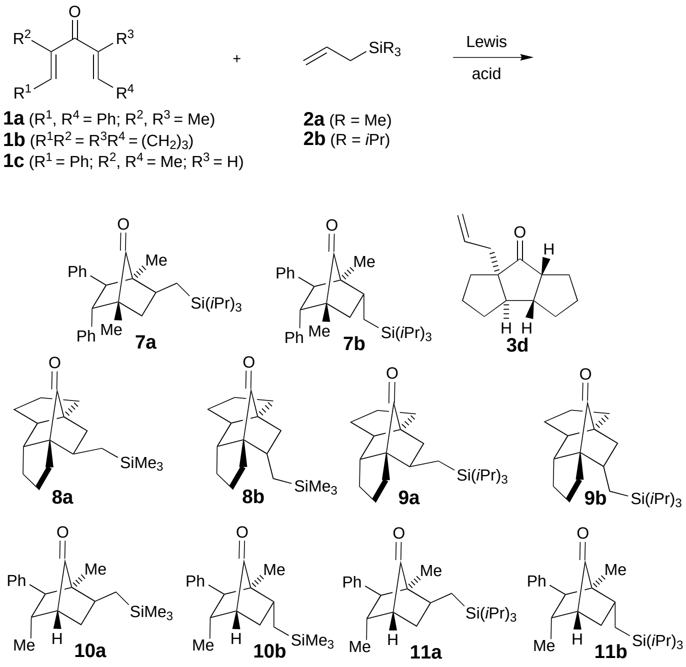
zwitterion **6a** or ring closure with concomitant sila-Wagner-Meerwein shift, respectively. Proton and carbon NMR data were more consistent with structure **4a** (with the indicated stereochemistry), and further support came from the unambiguous assignment of closely related structures by X-ray diffraction analysis (see below). Notably, no products derived from either the simple Nazarov cyclization of **1a** or the Hosomi–Sakurai addition of **2a** to **1a**[11] were observed.

The formation of **4a** entails three successive carbon–carbon bond-forming steps: a) electrocyclic closure of the dienone–Lewis acid complex to generate the oxyallyl intermediate; b) nucleophilic attack of the allylsilane γ carbon atom at one of the oxyallyl termini to produce an adduct with a boron enolate and a silicon-stabilized carbocation; and c) collapse of this zwitterion to the bridged bicyclic product. The majority of the simple allylated material (**3a** + **3b**, 30%) resulted from **6b**, which was formed by the allylsilane approaching from the face opposite the adjacent phenyl group. In contrast, **4a** derives from **6a**, which is formed by the apparent attack of the allylsilane from the same face as the adjacent phenyl ring. The failure to observe any bicyclic products resulting from **6b** may be a result of unfavorable nonbonded interactions in the transition state (**A**) for ring closure.

These promising results prompted a more comprehensive examination of this novel domino process (Table 1). Preliminary screening of conditions established that $BF_3 \cdot OEt_2$ and $SnCl_4$ gave superior yields and selectivity, and subsequent reactions were carried out with only these Lewis acids. Variation of the stoichiometry was also informative: while the initial result was obtained using ten equivalents of allylsilane to ensure efficient trapping of the oxyallyl intermediate, it quickly became apparent that nearly comparable results were obtained with as little as two equivalents (entries 1 vs. 2, 5 vs. 6, 7 vs. 8, 10 vs. 11, and 12 vs. 13). We were interested in examining the effect of a bulkier silyl group, as this change was expected to suppress desilylation and favor the [3+2] pathway.[12] In the event, treatment of **1a** with allyltriisopropylsilane (**2b**) yielded approximately 50% of the [3+2] adduct with either $BF_3 \cdot OEt_2$ or $SnCl_4$, with little or no accompanying allylation product **3** (entries 4–6). A remarkable dependence of the stereochemistry on the Lewis acid used was noted in this case: while $BF_3 \cdot OEt_2$ led to a 1:1 mixture of diastereomers **7a** and **7b**, $SnCl_4$ gave exclusively *exo* isomer **7b**, whose structure was unambiguously determined by X-ray diffraction analysis. As noted below, this was also seen in a number of other cases.

The nature of the dienone was also probed. Dienone **1a** was known to undergo rapid electrocyclization even at low temperature, and we wondered whether a less reactive dienone could also be used in this domino process. To that end, we next examined the behavior of dicyclopentenyl ketone (**1b**)[10c] with **2a** and **2b** (entries 7–13).[13] Cyclization of **1b** in the presence of **2a** and $BF_3 \cdot OEt_2$ provided the [3+2] adduct **8a** in 35% yield as a single (*endo*) diastereomer, while use of $SnCl_4$ led to diastereomeric **8b** in low yield. On the other hand, the corresponding [3+2] adducts **9a** and **9b** were obtained in 65 and 91% yields, respectively (entries 10–13), with allylsilane **2b**. The structure of **9b** was unambiguously determined by X-ray crystallography, and strong support for the structure assigned to **9a** was obtained through two-dimensional NMR analysis. As in the case of **8a** and **8b**, the stereochemistry of the [3+2] adducts was completely dependent upon the choice of Lewis acid. The initial attack of the allylsilane occurs from the less-hindered face (Scheme 2, path a) during the formation of **8a**, **b** and **9a**, **b**, which is in contrast to the results obtained with **1a**. This is likely a consequence of the unfavorable *trans*-diquinane ring fusion that would result from an attack analogous to that in the monocyclic cases (path b). However, a *trans* ring fusion is then

Table 1. Dienone + allylsilane domino [3+2] trapping reactions.[a]

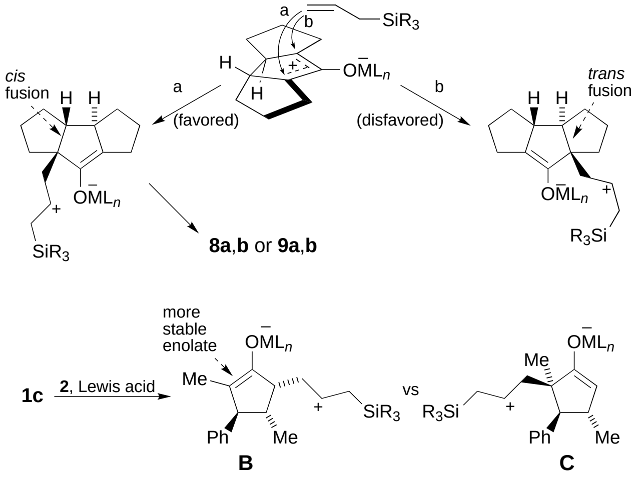


Entry	Dienone	Allylsilane (equiv)	Lewis acid	Products (% yield)[b]
1	**1a**	**2a** (10)	$BF_3\cdot OEt_2$	**3a–c** (43) + **4a** (49)
2	**1a**	**2a** (2)	$BF_3\cdot OEt_2$	**3a–c** (35) + **4a** (42)
3	**1a**	**2a** (10)	$SnCl_4$	**3a-c** (29) + **4a** (29)
4	**1a**	**2b** (5)	$BF_3\cdot OEt_2$	**3a** (28) + **7a** (25) + **7b** (25)
5	**1a**	**2b** (5)	$SnCl_4$	**7b** (51)
6	**1a**	**2b** (2)	$SnCl_4$	**7b** (47)
7	**1b**	**2a** (10)	$BF_3\cdot OEt_2$	**3d** (30) + **8a** (35)
8	**1b**	**2a** (2)	$BF_3\cdot OEt_2$	**3d** (30) + **8a** (32)
9	**1b**	**2a** (10)	$SnCl_4$	**3d** (35) + **8b** (10)
10	**1b**	**2b** (10)	$BF_3\cdot OEt_2$	**9a** (65)
11	**1b**	**2b** (2)	$BF_3\cdot OEt_2$	**9a** (60)
12	**1b**	**2b** (5)	$SnCl_4$	**9b** (90)
13	**1b**	**2b** (2)	$SnCl_4$	**9b** (91)
14	**1c**	**2a** (10)	$BF_3\cdot OEt_2$	**10a**
15	**1c**	**2a** (10)	$SnCl_4$	**10a** (37) + **10b** (28)
16	**1c**	**2b** (10)	$BF_3\cdot OEt_2$	**11a** (72)
17	**1c**	**2b** (10)	$SnCl_4$	**11a** (38) + **11b** (61)

[a] See Experimental Section for a typical procedure. Further details can be found in the Supporting Information. [b] Yields of isolated products after chromatography.

unavoidable in the final ring closure. In light of the strain inherent in the products, the efficiency with which **9a** and **9b** are formed is quite remarkable.

Finally, the behavior of unsymmetrical dienone **1c** was studied to probe the regiochemical preferences of the domino process (entries 14–17). Cyclization in the presence of **2a** or **2b** using $BF_3\cdot OEt_2$ led to the exclusive formation of *exo* products **10a** and **11a**, respectively, while $SnCl_4$ provided mixtures of *endo* and *exo* isomers with either allylsilane. In all four examples the initial attack on the unsymmetrical oxyallyl system occurred at the less-substituted terminus. On the basis of related intermolecular trapping reactions involving photochemically generated oxyallyls, we had expected attack to occur preferentially at the more-substituted end because of the greater positive-charge density.[14] However, exclusive bond formation at the less substituted end of the allyl system is consistent with earlier observations by Noyori et al.,[15] and can be rationalized in terms of enolate stability, with preferred formation of the more substituted isomer **B** rather than **C** (Scheme 2). As with **1a**, the allylsilane approached the oxyallyl from the same face as the larger (methyl) group on the neighboring carbon atom.



Scheme 2.

We have described the first examples of intermolecular trapping of the Nazarov oxyallyl intermediate by carbon nucleophiles. This transformation creates three new carbon–carbon bonds and up to five contiguous stereocenters during the construction of densely functionalized bicyclo[2.2.1]heptanones from simple dienone and allylsilane precursors. Regioselectivity is complete in the case of an unsymmetrical dienone, as is the stereoselectivity of the initial trapping step in all cases. The final ring-closure step is highly sensitive to the Lewis acid used in the electrocyclization: in several cases complete selectivity for *exo*- or *endo*-disposed CH_2SiR_3 groups could be achieved by use of either $BF_3\cdot OEt_2$ or $SnCl_4$. Further studies of the scope of this process and the origins of the Lewis acid-dependence of the stereochemical outcome are underway and will be disclosed in due course.

Experimental Section

Cyclization of **1a** in the presence of **2a** (representative procedure): CH_2Cl_2 (10 mL) and **2a** (217 mg, 1.9 mmol) were added to a dry 50-mL round-bottom flask equipped with a magnetic stir bar, nitrogen inlet, and rubber septum, and the resulting solution was cooled to –78 °C. $BF_3\cdot OEt_2$ (30 mg, 0.21 mmol) was added by syringe followed by the dropwise addition of a solution of **1a** (50 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) by cannula. The resulting slightly yellow-brown solution was allowed to slowly warm to 0 °C and the reaction was quenched by the addition of H_2O (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a colorless oil which was purified by flash chromatography (silica gel, hexanes/EtOAc 30/1 → 25/1 → 20/1 → 15/1) to provide **4a** (35 mg, 49 %) as a white solid, **3a** (12 mg, 21 %) as a white solid and an inseparable mixture of **3b** and **3c** (~2/3; 12 mg, 21 %) as a colorless oil. For purposes of characterization, **3c** could be obtained in pure form by carrying out the reaction using $TiCl_4$ in place of $BF_3\cdot OEt_2$. **4a**: m.p. 115–116 °C; $R_f = 0.56$ (hexanes/EtOAc 4/1); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.39-7.01$ (m, 10H), 3.30 (d, ^3J(H,H) = 7.2 Hz, 1H), 3.12 (dd, ^3J(H,H) = 7.2, ^4J(H,H) = 2.2 Hz, 1H), 2.21 (dd,

^{2}J(H,H) = 12.9, ^{3}J(H,H) = 10.1 Hz, 1 H), 2.15–2.09 (m, 1 H), 1.02 (s, 3 H), 0.87 (ddd, ^{2}J(H,H) = 13.0, ^{3}J(H,H) = 4.7, ^{4}J(H,H) = 2.1 Hz, 1 H), 0.83 (dd, ^{2}J(H,H) = 14.1, ^{3}J(H,H) = 2.4 Hz, 1 H), 0.70 (s, 3 H), 0.26 (dd, ^{2}J(H,H) = 13.9, ^{3}J(H,H) = 13.3 Hz, 1 H), 0.04 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 219.5, 143.6, 138.3, 129.5, 128.6, 128.5, 128.5, 127.2, 126.9, 55.8, 55.6, 51.6, 48.3, 40.1, 35.0, 21.6, 14.4, 10.6, –0.3; IR (thin film): $\tilde{\nu}$ = 1756.8 cm^{-1}; elemental analysis calcd for $C_{25}H_{32}OSi$: C 79.71, H 8.58; found: C 79.63, H 8.57. **3a**: m.p. 80–81 °C; R_f = 0.50 (hexanes/EtOAc 4/1); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.23–7.11 (m, 10 H), 5.87–5.73 (m, 1 H), 5.28–5.22 (m, 2 H), 3.69 (d, ^{3}J(H,H) = 12.2 Hz, 1 H), 3.25 (dd, ^{3}J(H,H) = 12.0, 12.0 Hz, 1 H), 2.53 (dddd, ^{2}J(H,H) = 14.3, ^{3}J(H,H) = 5.6, ^{4}J(H,H) = 1.7, 1.7 Hz, 1 H), 2.26 (dq, ^{3}J(H,H) = 11.7, 6.9 Hz, 1 H), 2.11 (dd, ^{2}J(H,H) = 14.4, ^{3}J(H,H) = 13.9 Hz, 1 H), 1.13 (d, ^{3}J(H,H) = 6.8 Hz, 3 H), 0.76 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 221.5, 140.9, 137.4, 134.6, 129.4, 128.8, 128.3, 127.9, 127.0, 126.8, 119.5, 53.5, 53.4, 52.8, 50.8, 41.2, 20.6, 13.2; IR (thin film): $\tilde{\nu}$ = 1734 cm^{-1}; elemental analysis calcd for $C_{22}H_{24}O$: C 86.78, H 7.96; found: C 86.64, H 8.07. **3b**: R_f = 0.46 (hexanes/EtOAc 4/1); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.28–7.11 (m, 10 H), 5.85–5.70 (m, 1 H), 5.30–5.24 (m, 2 H), 4.15 (dd, ^{3}J(H,H) = 13.2, 8.3 Hz, 1 H), 3.93 (d, ^{3}J(H,H) = 13.0 Hz, 1 H), 2.84 (dq, ^{3}J(H,H) = 8.1, 8.0 Hz, 1 H), 2.55 (dddd, ^{2}J(H,H) = 14.2, ^{3}J(H,H) = 5.1, ^{4}J(H,H) = 1.6, 1.6 Hz, 1 H), 2.11 (dd, ^{2}J(H,H) = 14.0, ^{3}J(H,H) = 9.0 Hz, 1 H), 0.83 (s, 3 H), 0.74 (d, ^{3}J(H,H) = 7.8 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 223.3, 138.4, 137.7, 135.0, 129.2, 129.0, 128.4, 126.9, 126.5, 119.4, 54.4, 47.1, 46.6, 44.8, 40.4, 20.7, 12.0 (one carbon resonance is obscured by an overlapping resonance from **3c**). **3c**: m.p. 96 °C; R_f = 0.46 (hexanes/EtOAc 4/1); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.28–7.11 (m, 10 H), 5.51 (dddd, ^{3}J(H,H) = 16.8, 10.0, 7.3, 7.3 Hz, 1 H), 4.97 (dddd, ^{3}J(H,H) = 10.0, ^{2}J(H,H) = 2.1, ^{4}J(H,H) = 1.0, 1.0 Hz, 1 H), 4.86 (dddd, ^{3}J = 16.8, ^{2}J(H,H) = 2.2, ^{4}J(H,H) = 1.4, 1.1 Hz, 1 H), 3.44 (dd, ^{3}J(H,H) = 11.9, 11.2 Hz, 1 H), 3.43 (d, ^{3}J(H,H) = 11.9 Hz, 1 H), 2.38 (dq, ^{3}J(H,H) = 11.2, 6.8 Hz, 1 H), 2.13 (dd, ^{2}J(H,H) = 14.1, ^{3}J(H,H) = 7.1 Hz, 1 H), 1.72 (dddd, ^{2}J(H,H) = 14.1, ^{3}J(H,H) = 7.3, ^{4}J(H,H) = 1.1, 1.1 Hz, 1 H), 1.22 (s, 3 H), 1.19 (d, ^{3}J(H,H) = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 220.7, 141.0, 136.7, 133.6, 129.4, 128.8, 128.3, 127.9, 127.1, 127.0, 118.2, 58.9, 53.2, 52.3, 50.4, 37.8, 22.1, 13.7; IR (thin film): $\tilde{\nu}$ = 1734.7 cm^{-1}; elemental analysis calcd for $C_{22}H_{24}O$: C 86.78, H 7.96; found: C 86.71, H 8.01.

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Reaction of [{PhP(Se)(μ-Se)}$_2$] with Dialkyl Cyanamides: X-ray Crystal Structures of the Phosphorus-Containing Triselenapentalenes $[\mathrm{Me_2N{-}C(Se){=}N}]_2\mathrm{P(Se)Ph}$ and $[\mathrm{O(CH_2CH_2)_2N{-}C(Se){=}N}]_2\mathrm{P(Se)Ph}$**

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The chemistry of phosphorus–selenium heterocycles $(RP)_xSe_y$ (R = alkyl or aryl), which are generally prepared by oxidation of the parent homocyclic polyphosphanes $(RP)_n$ with stoichiometric quantities of elemental selenium, has received scant attention.[1–7] The studies undertaken on the reactivity of these molecules have to date been directed towards the development of new selenating reagents for the transformation of carbonyl groups in organic molecules to selenocarbonyls.[1, 8] In this regard, an analogue is sought of the commercially available 2,4-bis(p-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide [{(p-MeOC$_6$H$_4$)P(S)(μ-S)}$_2$] (Lawesson's reagent), a valuable tool for the conversion of carbonyl compounds to their thiocarbonyl counterparts.[9]

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