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Radical 1,2-O→C Transposition for Conversion of Phenols into Benzoates by O-Neophyl Rearrangement/Fragmentation Cascade

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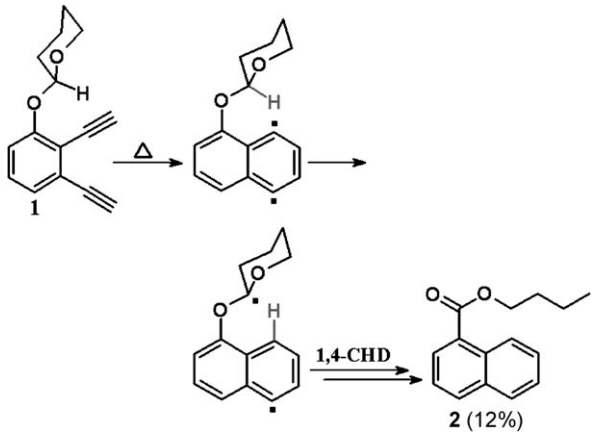
Both phenols and benzoic acid derivatives are among the most common organic functional groups in organic chemistry. The transformation of an aryl alcohol into an aryl carboxylic acid derivative requires substitution of the phenol oxygen with a carbon atom, which is usually accomplished by metal-catalyzed carbonylation.[1] A metal-free O→C transposition reaction designed to convert phenols or their derivatives into benzoate esters would be a useful alternative to this important class of organic molecules.

This work has been inspired by our attempts to unravel the mechanisms of fragmentation of the natural enediyne antibiotic esperamycin A_1 as the result of its activation to the Bergman cyclization.[2] In our studies, we have discovered a variety of radical rearrangements that follow Bergman cyclization in enediynes equipped with acetal rings, mimicking the carbohydrate moiety of natural enediyne antibiotics. A particularly interesting finding was that of a radical cascade proceeding by an O-neophyl rearrangement, which transposes the O and C atoms of the substituent (Scheme 1).[3] Although the observed yield of the rearranged benzoic ester **2** from enediyne **1** was low, this product formation suggested the possibility of the rational design of a radical process that would allow a useful transformation of phenols into benzoate esters.

Intrigued by these observations, we decided to develop a more efficient radical cascade that improves on the transformation illustrated in Scheme 1. Several elements were important for the structural design. First, the ideal sequence should start from a functional group that can be readily prepared from phenols. Second, the design should incorporate an efficient step that selectively creates a radical at the correct carbon atom from the above functional group in either an intra- or intermolecular manner. Third, the radical should be sufficiently reactive to initiate the key 1,2 O→C transposition through an *ipso* attack at the aromatic ring, followed by C–O bond cleavage (O-neophyl rearrangement).[4,5] For this purpose, substituents X and Z should not deactivate the radical center through excessive stabilization and should not participate in a premature β-scission step (Scheme 2). Finally, the transposed radical should possess a weak C–X bond which can undergo an efficient terminating β-scission step that renders the overall process irreversible, as shown in Scheme 2.[6]



Scheme 1. O→C Radical transposition triggered by the Bergman cyclization of enediynes.

The final fragmentation step is important because most O-neophyl rearrangement examples in the literature proceed in the opposite direction in which alkoxy radicals rearrange to more stable carbon radicals.[7,8] To the best of our knowledge, there is only one literature example in which the rearrangement occurs in the direction we observed in the reaction of enediyne **1**—from a carbon-centered radical to an oxygen-centered radical.[9]

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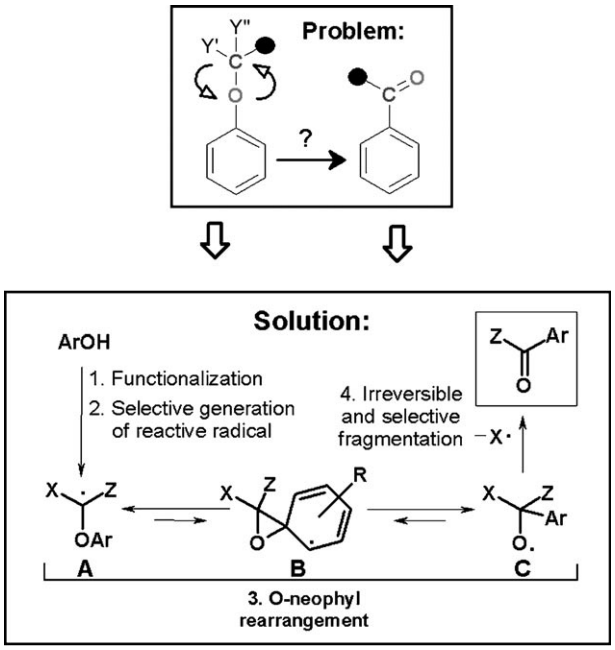


Scheme 2. Suggested design of an efficient radical 1,2 O→C transposition cascade.

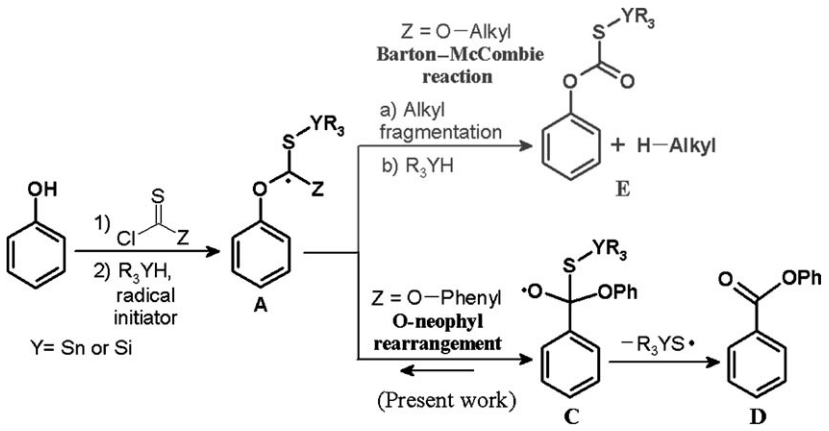
A plausible approach to the selective generation of an aryloxy radical precursor **A** for the rearrangement step is provided by the initial steps of the Barton–McCombie deoxygenation of alcohols (Scheme 3).[10] This method involves the reaction of thiocarbonates with Si- or Sn-centered radicals. Due to thiophilicity of these radicals, they regioselectively attack the sulfur atom of the C=S moiety. Not only does this attack provide the appropriate carbon-centered radical, but it also forms a weak C–S bond positioned for β-scission at the final, equilibrium-shifting fragmentation.

However, in order for the carbon radical to undergo O-neophyl rearrangement, the Barton–McCombie pathway has to be rerouted away from the fast fragmentation step **A**→**E** (Scheme 3). We decided to test whether the premature fragmentation step can be avoided by replacing the alkyl group R with an aromatic substituent. Not only does an aryloxy group have a stronger C(sp^2)–O bond, but the fragmentation would also result in a relatively unstable sp^2 radical.

Initially, we tested our design by treating diphenyl thiocarbonate with Bu_3SnH and AIBN in benzene at reflux. Only traces of the desired product (**D**) were detected by ^1H NMR spectroscopy and GC, even after heating at 135 °C in a sealed tube, with very low conversion of starting material. However, when the reaction was performed using triethylsilane (TES)[11] and di-*tert*-butyl peroxide (TOOT) at 135 °C in benzene, the proposed O→C transposition cascade indeed proceeded to afford 59 % of phenyl benzoate.

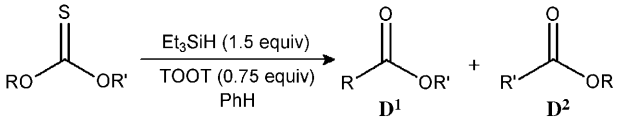
To expand the scope of this process and to gain a deeper insight into its mechanism, we investigated substituent effects on the efficiency and selectivity of the new reaction. Thus, several diaryl thiocarbonates were synthesized from thiophosgene and the corresponding phenols in 75–90 % yield. In full agreement with the proposed mechanism, both OMe and CN substituents facilitate the rearrangement (Table 1, entries 2, 3, and 4), indicating the development of radical character at the *para* position of the migrating aryl group in the rate-limiting step.[12] High yields (≥80 %) of rearranged products were obtained when at least one of the aryl groups was equipped with a radical-stabilizing substituent. On the other hand, lower yields and selectivities were observed for fluoro-substituted aryl thiocarbonate (Table 1, entry 5) and pyridinyl substituted thiocarbonate (Table 1, entry 8). We will show (see below) that this correlation of reactivity and selectivity is not surprising. For comparison, we also included alkyl-substituted thiocarbonates and observed fragmentation along the Barton–McCombie pathway under the same reaction conditions (Table 1, entries 9 and 10).

We also investigated whether other functional groups in thiocarbonates could react under these conditions, opening the possibility for further cascade transformations. Unlike nitro-substituted thiocarbonate (Table 1, entry 7), which provided a complex reaction mixture, the *p*-bromo-substituted reactant (Table 1, entry 6) was converted into biphenyl derivatives of the rearranged products, **D**[3] (12 %) and **D**[4] (25 %) (Scheme 4). The biphenyl moiety formation can be readily explained by abstraction of the *p*-bromine atom by the TES radical followed by the reaction of the resulting aryl radical with benzene solvent (radical aromatic substitution, RAS[13]). To investigate the two possible pathways for the formation of **D**[3] and **D**[4] (Scheme 4), we studied the reaction of the bromothiocarbonate at lower conversions and obtained 13 % of **D**[1]



Scheme 3. Rerouting the Barton–McCombie reaction to the O-neophyl rearrangement pathway for the conversion of aryl alcohols into benzoate esters.

Table 1. Results of O-neophyl rearrangement/fragmentation reaction of diaryl thiocarbonates.



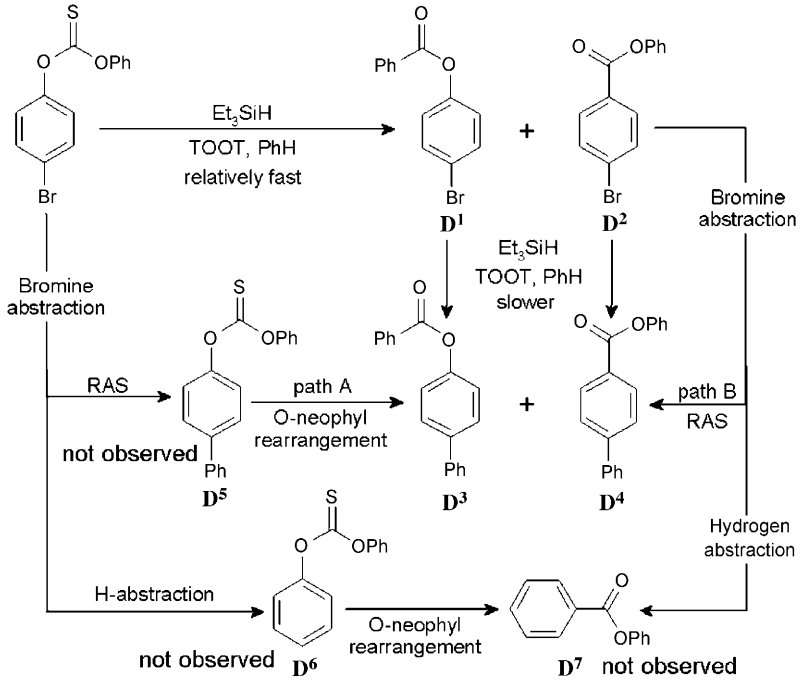
Entry	R	R′	t [h] (135 °C)	Yield $\mathbf{D^1}$ [%]	Yield $\mathbf{D^2}$ [%]
1	Ph	Ph	2	59	NA
2	*p*-MeOPh	*p*-MeOPh	2	93	NA
3	Ph	*p*-MeOPh	2	30	61
4	Ph	*p*-CNPh	1.5	16	63
5	Ph	*p*-FPh	2	31	31
6	Ph	*p*-BrPh[a,b]	4	19	27
7	Ph	*p*-NO_2Ph	2–5	[c]	–
8	Ph	3-Pyridinyl[a]	4	30	34
9	Ph	Et[d]	2	[e]	NA
10	Ph	*p*-MeOPh-Pr[d,f]	2	[e,g]	NA

[a] 3 equiv of Et_3SiH and 1.5 equiv of TOOT were used for full conversion of starting material. [b] Two additional products were formed besides $\mathbf{D^1}$ and $\mathbf{D^2}$. [c] A complicated mixture was obtained. [d] TTMSS was used since no reaction was observed with TES. [e] 100% alkyl fragmentation (Barton–McCombie). [f] 1-(*p*-Methoxyphenyl)propyl group. [g] *p*-Propyl anisole was formed in 60% yield.

Table 2. Reaction of bromothiocarbonate with different equivalents of radical reagents.

	Et_3SiH (equiv TOOT)	t [h]	Yield [%] $\mathbf{D^1}$	$\mathbf{D^2}$	$\mathbf{D^3}$	$\mathbf{D^4}$
6 (*p*-BrPh)	1.5 (0.75)	2[a]	≈5	≈8	0	0
	1.5 (0.75)	4[b]	14	24	2	4
	3 (1.5)	4	19	27	12	25
	4 (2)	10[c]	0	0	21	48
11 ($\mathbf{D^1}$+$\mathbf{D^2}$) (1:1.4)	6 (3)	3	18	17	14	28

[a] 15% Conversion of starting material. [b] 50% Conversion of starting material. [c] Traces of phenyl benzoate were detected by NMR.



Scheme 4. Coupled radical cascades in the reaction of bromo-substituted thiocarbonate (Table 1, entry 6) with the TES radical.

and $\mathbf{D^2}$ as the only products (Table 2). Upon additional heating, 38% of $\mathbf{D^1}$ and $\mathbf{D^2}$ were formed in addition to 6% of $\mathbf{D^3}$ and $\mathbf{D^4}$. These experiments suggest that the O-neophyl rearrangement pathway is more than six times faster than bromine abstraction and that path B (Scheme 4) serves as the major route to the formation of the biphenyl products $\mathbf{D^3}$ and $\mathbf{D^4}$. When a mixture of isolated bromoesters $\mathbf{D^1}$ and $\mathbf{D^2}$ was subjected to the same conditions, biphenyls were the only products obtained in the same ratio. It is noteworthy that the total yield of the two products in this one-pot sequence approaches 70%. Hence, this one-pot radical sequence reaction of rearrangement can be expanded to the synthesis of modified biphenyl esters from thiocarbonates of simple and commercially available bromophenols.

To gain further insight into the observed experimental trends, we carried out DFT calculations of the proposed reaction pathway for selected substrates. All structures were fully optimized at the UB3LYP/6-31+G** level by using Gaussian 03 software.[14] Figure 1 shows the calculated potential energy surface of the possible O-neophyl rearrangements and fragmentation pathways of thiocarbonates. As shown in Table 3, the radical addition step for diaryl thiocarbonates is highly exothermic (22-24 kcal mol^{-1}) with a barrier as low as ≈3 kcal mol^{-1}. However, the activation barrier for the subsequent O-neophyl rearrangement step is relatively high (23–25 kcal mol^{-1}), making the rearrangement kinetically competitive with the backward fragmentation step. The relative inefficiency of the rearrangement step is the likely reason for the high temperatures and excess of reagents needed for achieving high conversions. The significant barrier magnitude stems from efficient anomeric radical stabilization of the carbon radical intermediate through two n(O)→n(C) and one n(S)→n(C) interactions. This result agrees well with the relative values for previously calculated barriers for similar rearrangements of carbon radicals with varying degrees of stabilization.[3a,15] In addition to the electronic factors, steric repulsion exerted by the bulky OAr and SY groups can contribute to raising the energy of the three-membered transition state.

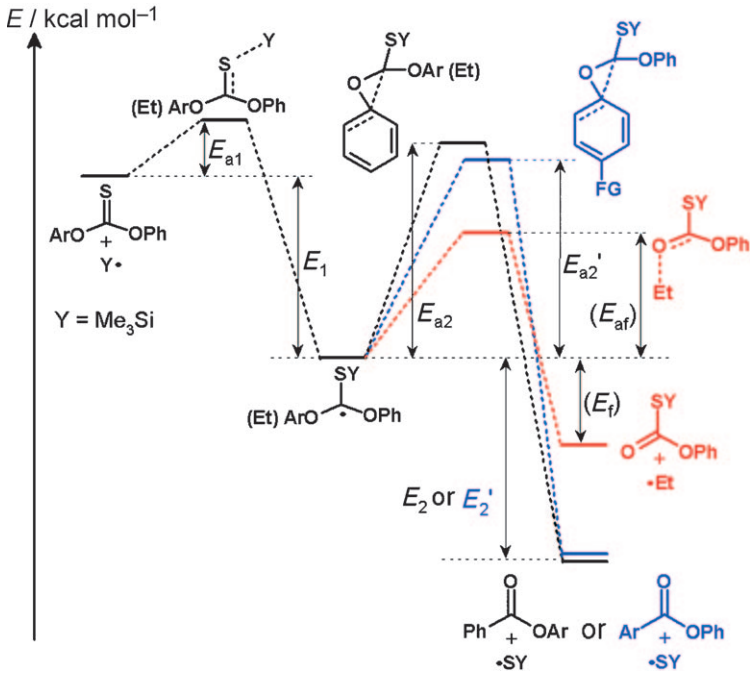


Figure 1. Calculated potential energy diagrams for O-neophyl rearrangement and fragmentation pathways (black: O-neophyl rearrangement of diaryl thiocarbonate at the phenyl group; blue: O-neophyl rearrangement of diaryl thiocarbonate at the *p*-substituted aryl group; red: Barton–McCombie fragmentation). See Table 3 for the calculated energy values.

Table 3. Computational analysis of the rearrangements of diaryl thiocarbonates at the UB3LYP/6-31+G** level.[a]

	E_{a1} [kcal mol^{-1}]	E_1 [kcal mol^{-1}]	E_{a2} (E_{af}) [kcal mol^{-1}]	E_2 (E_f) [kcal mol^{-1}]	E_{a2}'	E_2'
1	3.2	−23.1	24.8	−26.7	NA[b]	NA[b]
3	3.1	−22.3	24.4	−27.3	23.9	−29.3
4	3.0	−24.5	24.9	−25.9	23.2	−23.7
5	–	−22.9	24.5	−27.0	24.4	−27.8
6	–	−23.7	24.4	−26.5	24.1	−27.0
8	–	−23.5	24.9	−26.8	24.5	−26.6
9	4.5	−18.7	22.0 (13.1)	−30.0 (−9.1)	NA[b]	NA[b]

[a] Entries are relative to Table 1. Energies are given in kcal mol^{-1} relative to the previous intermediate in the reaction path. See the Supporting Information for computational details. [b] NA = not applicable.

In a number of earlier computational[3a,15] and experimental[16] studies, O-neophyl rearrangements have been found to proceed via a three-membered radical intermediate **B**. However, our calculations suggest that the O-neophyl rearrangement/fragmentation pathway is a concerted process for the systems presented herein on the UB3LYP/6-31+G** energy surface. Excluding *p*-CN substituted thiocarbonate (entry 4), neither of the radical intermediates **B** or **C** (Scheme 2) was located for any of the above diaryl thiocarbonates. Instead, all attempts for their structural optimizations lead to the final rearranged/fragmented products (**D**+YS•). On the other hand, a three-membered dearomatized radical intermediate (**B**) was located for the *p*-CN thiocarbonate probably due to additional radical stabilization provided by the extended conjugation of the cyano group. Overall, as it was designed, the reaction is efficiently driven by the high exothermicity of the final step (≈50 kcal mol^{-1} below the reactants thiocarbonate and the silyl radical).

Our experimental substituent effects agree with the lower values for the computed activation barriers for the rearrangement of substituted aryl groups (Figure 1, blue path). In particular, lower barriers were obtained for aryl rings with radical stabilizing groups (OMe and CN) at the *para* position. On the other hand, the rearrangement at the phenyl group of monosubstituted diaryl thiocarbonates (Figure 1, black path) has essentially the same activation barrier as the parent diphenyl thiocarbonate (Table 3, entry 1). The sufficient accuracy of the computational methods is illustrated by the observed lack of differences for the competing rearrangement directions of those thiocarbonates (with 4-fluorophenyl, 4-bromophenyl, and 3-pyridinyl groups) that do not show significant experimental selectivity. It is noteworthy that the rearrangement barrier is considerably higher than the barrier of Barton–McCombie fragmentation for alkyl substituted substrates (Figure 1, red path). This difference would kinetically favor the Barton–McCombie fragmentation pathway when this path is available (Table 1, entries 9 and 10).

In summary, we found that this radical cascade can be used as a convenient procedure for the transformation of phenols into esters of the respective aromatic carboxylic acids. O-Neophyl rearrangement from a C-centered radical to an O-centered radical is rendered irreversible when it is coupled to a subsequent highly exothermic fragmentation.

Experimental Section

General procedures for the synthesis of symmetrical thiocarbonates: Phenol (2.4 mmol) was dissolved in 0.3 M aqueous NaOH (8 mL) and added to a solution of $CSCl_2$ (1.2 mmol) in CH_2Cl_2 (10 mL). The reaction solution (two layers) was stirred vigorously for 2 h and then diluted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography to afford the corresponding thiocarbonate.

General procedures for the synthesis of nonsymmetrical thiocarbonates

Procedure A: The first phenol (1.2 mmol) was dissolved in 0.3 M aqueous NaOH (4 mL) and added to a solution of $CSCl_2$ (1.8 mmol) in CH_2Cl_2 (10 mL). The two layers were stirred vigorously for 1 h. The reaction mixture was diluted with CH_2Cl_2 and washed with brine. The organic

layer was dried with Na_2SO_4. The solvent and excess $CSCl_2$ were removed under reduced pressure. The reaction mixture was then redissolved in CH_2Cl_2 (10 mL). The second phenol (1.2 mmol) was then dissolved in 0.3 M aqueous NaOH (4 mL) and added to the above solution of the reaction mixture in CH_2Cl_2 and stirred for 2 h. The reaction was then worked up in the same way as before and purified by column chromatography to afford the corresponding thiocarbonate.

Procedure B: The first phenol (1.2 mmol) and $CSCl_2$ (1.8 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred at 0 °C. Neat pyridine (1.5 mmol) was then added dropwise at 0 °C. The reaction mixture was left to warm to room temperature for 15 min with stirring, before it was diluted with CH_2Cl_2 and washed with brine. The organic layer was dried with Na_2SO_4. The solvent and excess $CSCl_2$ were removed under reduced pressure. The reaction mixture and the second phenol (1.2 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred at room temperature. Neat pyridine (1.5 mmol) was then added dropwise to the reaction mixture at room temperature. The reaction mixture was stirred for 30 min, worked up in the same way as described above, and purified by column chromatography to afford the corresponding thiocarbonate.

General procedure for the O-neophyl rearrangement/fragmentation reaction: Et_3SiH (0.052 mmol) and TOOT (0.026 mmol) were added to a solution of the starting thiocarbonate (0.035 mmol) in benzene. The solution was then purged with N_2 for 15 min, sealed in an Ace Glass pressure tube or thick-walled Pyrex tube, and heated at 135 °C in an oil bath. The solvent was evaporated and the product was purified by chromatography.

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Keywords: alkynes · phenols · radical fragmentation · rearrangement · thiocarbonates

[1] C. F. J. Barnard, *Organometallics* **2008**, *27*, 5402; A. Brennführer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114; R. Lou, M. VanAlstine, X. Sun, M. P. Wentland, *Tetrahedron Lett.* **2003**, *44*, 2477; O. Rahman, T. Kihlberg, B. Långström, *J. Org. Chem.* **2003**, *68*, 3558; O. Rahman, T. Kihlberg, B. Långström, *J. Chem. Soc. Perkin Trans. 1* **2002**, 2699; U. Gerlach, T. Wollmann, *Tetrahedron Lett.* **1992**, *33*, 5499; S. Cacchi, A. Lupi, *Tetrahedron Lett.* **1992**, *33*, 3939; R. E. Dolle, S. J. Schmidt, L. I. Kruse, *J. Chem. Soc. Chem. Commun.* **1987**, 904; S. Cacchi, P. G. Ciattini, E. Morera, G. Ortar, *Tetrahedron Lett.* **1986**, *27*, 3931.

[2] D. R. Langley, J. Golik, B. Krishnan, T. W. Doyle, D. L. Beveridge, *J. Am. Chem. Soc.* **1994**, *116*, 15.

[3] a) A. Baroudi, J. Mauldin, I. V. Alabugin, *J. Am. Chem. Soc.* **2010**, *132*, 967; for our preliminary work on the effect of *ortho* substituents, see: T. A. Zeidan, M. Manoharan, I. V. Alabugin, *J. Org. Chem.* **2006**, *71*, 954; T. Zeidan, S. V. Kovalenko, M. Manoharan, I. V. Alabugin, *J. Org. Chem.* **2006**, *71*, 962; J. F. Kauffman, J. M. Turner, I. V. Alabugin, B. Breiner, S. V. Kovalenko, E. A. Badaeva, A. Masunov, S. Tretiak, *J. Phys. Chem. A* **2006**, *110*, 241; I. V. Alabugin, M. Manoharan, *J. Phys. Chem. A* **2003**, *107*, 3363; I. V. Alabugin, M. Manoharan, S. V. Kovalenko, *Org. Lett.* **2002**, *4*, 1119.

[4] D. E. Falvey, B. S. Khambatta, G. B. Schuster, *J. Phys. Chem.* **1990**, *94*, 1056; for a topologically similar anionic rearrangement of 2-benzyloxypyridines, see: J. Yang, G. B. Dudley, *J. Org. Chem.* **2009**, *74*, 7998.

[5] For another example of the use of oxygen in the C–C bond formation at the *ipso* position, see: S. F. Vasilevsky, D. S. Baranov, V. I. Mamatyuk, Y. V. Gatilov, I. V. Alabugin, *J. Org. Chem.* **2009**, *74*, 6143.

[6] A similar approach, which occurs through a five-membered transition state (1,4 O→C transposition), was used in the total synthesis of the aromatic series of podophyllotoxin, see: A. J. Reynold, A. J. Scott, C. I. Turner, M. S. Sherburn, *Am. Chem. Soc.* **2003**, *125*, 12108; J. Fischer, A. J. Reynold, L. A. Sharp, M. S. Sherburn, *Org. Lett.* **2004**, *6*, 1345.

[7] a) J. T. Banks, J. C. Scaiano, *J. Phys. Chem.* **1995**, *99*, 3527; b) R. L. Donkers, J. Tse, M. S. Workentin, *Chem. Commun.* **1999**, 135; c) K. Wietzerbin, J. Bernadou, B. Meunier, *Eur. J. Inorg. Chem.* **1999**, 1467.

[8] a) M. Kamata, K. Komatsu, *Tetrahedron Lett.* **2001**, *42*, 9027; b) R. L. Donkers, M. S. Workentin, *J. Am. Chem. Soc.* **2004**, *126*, 1688; c) C. S. Aureliano Antunes, M. Bietti, G. Ercolani, O. Lanzalunga, M. Salamone, *J. Org. Chem.* **2005**, *70*, 3884; d) M. Bietti, M. Salamone, *J. Org. Chem.* **2005**, *70*, 10603; e) K. U. Ingold, M. Smeu, G. A. DiLabio, *J. Org. Chem.* **2006**, *71*, 9906.

[9] A. Ohno, N. Kito, Y. Ohnishi, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 467.

[10] a) D. H. R. Barton, S. W. McCombie, *J. Chem. Soc. Perkin Trans. 1* **1975**, 1574; b) D. H. R. Barton, D. Crich, A. Löbberding, S. Z. Zard, *J. Chem. Soc. Chem. Commun.* **1985**, 646; c) D. H. R. Barton, D. Crich, A. Löbberding, S. Z. Zard, *Tetrahedron* **1986**, *42*, 2329; d) D. H. R. Barton, *Half a Century of Free Radical Chemistry*, Cambridge University Press, Cambridge, **1993**; e) S. Z. Zard, *Aust. J. Chem.* **2006**, *59*, 663.

[11] Tris(trimethylsilyl)silane (TTMSS: C. Chatgilialoglu, *Chem. Eur. J.* **2008**, *14*, 2310) was also found to be a possible source of Si-centered radicals. However, in our hands, the rearrangement has poor reproducibility with this silane.

[12] a) H. E. Zimmerman, R. D. Rieke, J. R. Scheffer, *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047; b) H. E. Zimmerman, I. V. Alabugin, W. Chen, Z. Zhu, *J. Am. Chem. Soc.* **1999**, *121*, 11930–11931.

[13] a) A. Núñez, A. Sànchez, C. Burgos, J. Alvarez-Builla, *Tetrahedron* **2004**, *60*, 6217; b) D. C. Harrowven, T. Woodcock, P. D. Howes, *Angew. Chem.* **2005**, *117*, 3967; *Angew. Chem. Int. Ed.* **2005**, *44*, 3899; c) D. P. Curran, A. I. Keller, *J. Am. Chem. Soc.* **2006**, *128*, 13706.

[14] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[15] a) M. Bietti, G. Ercolani, M. Salamone, *J. Org. Chem.* **2007**, *72*, 4515; b) M. Smeu, G. A. DiLabio, *J. Org. Chem.* **2007**, *72*, 4520.

[16] M. Salamone, M. Bietti, A. Calcagni, G. Gente, *Org. Lett.* **2009**, *11*, 2453.

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