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Substrate-Selective C−H Functionalization for the Preparation of Organosulfur Compounds from Crude Oil-Derived Components

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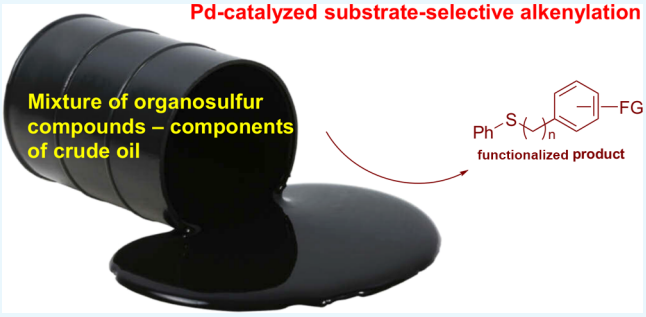
Supporting Information

ABSTRACT: The direct utilization of a natural feedstock in organic synthesis is an utmost challenge because the selective production of one product from a mixture of starting materials requires unprecedented substrate selectivity. In the present study, a simple and convenient procedure is evaluated for the substrate-selective alkenylation of a single component in a mixture of organosulfur compounds. Pd-catalyzed alkenylation of two-, three-, four-, and five-component mixtures of crude oil-derived sulfur species led to the exclusive C−H functionalization of only one compound. The observed remarkable substrate selectivity opens new opportunities for sustainable organic synthesis.



INTRODUCTION

Organosulfur derivatives represent a fundamental class of compounds in the chemical industry and organic synthesis. Worldwide, the volume of sulfur treated annually has increased to 70 100 000 metric tons.[1] Several emerging applications have been recently discovered, with a high demand for organosulfur derivatives in the fields of catalysis, nanotechnology, materials science, molecular electronics, asymmetric synthesis, biologically active compounds, and drug development.[2,3]

These cutting-edge applications stand in stark contrast with the obsolete procedures used for the production of organosulfur chemicals (Scheme 1). The majority of their production originates from processed fossil fuels (oil), in which organosulfur derivatives are present as contaminants.

Currently, a hydrodesulfurization procedure is used in petroleum refineries to remove sulfur, followed by conversion to H_2S and finally to elemental sulfur (Scheme 1). Organosulfur derivatives can be reconstructed (e.g., in the form of thiols) using reactions with organic halides followed by utilization in organic synthesis to produce the desired products. This procedure transforms the organosulfur species into elemental sulfur and then rebuilds the required products through a multistep synthesis. Obviously, the overall process is completely unsustainable from the point of view of the preparation of organosulfur products. The high energy consumption, cost inefficiency, waste generation, and environmental contamination are significant drawbacks.

For organic synthesis, we propose a more efficient approach involving a single-step procedure for the transformation of organosulfur components available in natural feedstock (Scheme 1). The idea is to functionalize only one component in the mixture at a time and to generate a single product. The separation of a functionalized product containing a polar group (e.g., COOR) from a nonpolar hydrocarbon mixture is a routine task. Therefore, a single product can be obtained from a mixture of starting materials. Achieving this challenging aim requires the development of catalytic systems with unprecedented substrate selectivity.

It should be pointed out that the proposed methodology is not an alternative for the hydrodesulfurization of fuels. Fine organic synthesis is the target for the methodology developed with the aim of sustainable synthesis of organic derivatives of sulfur via direct C−H functionalization of crude oil-derived starting materials.

C−H functionalization is one of the best approaches for introducing functional groups.[4] A variety of processes leading to the creation of new C−C and C−X bonds have been developed.[5−9] The efficiency of C−H alkenylation was improved by using a suitable directing group, which typically contains N and O heteroatoms. It is important to note that sulfur-only directing groups (without other heteroatoms) are quite rare.[8−12] However, successful C−H functionalization with distal and weakly coordinating groups is an advantage of Pd-catalyzed reactions.[13]

In the present study, we have evaluated the performance of a known C−H alkenylation reaction with sulfur atom as the directing group.[10] Amazingly, under optimized conditions, Pd-catalyzed C−H alkenylation of a mixture of organosulfur compounds can be performed with unprecedented substrate selectivity. These results demonstrated a promising potential of

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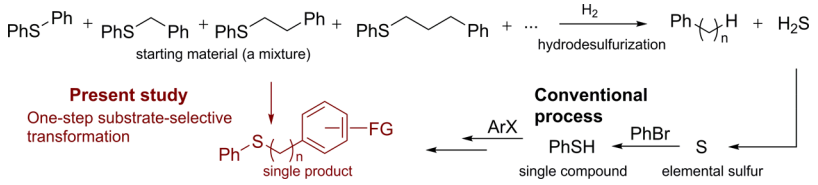
Scheme 1. Comparison of the Conventional Processing of Organosulfur Species from Natural Feedstock vs Direct Transformation



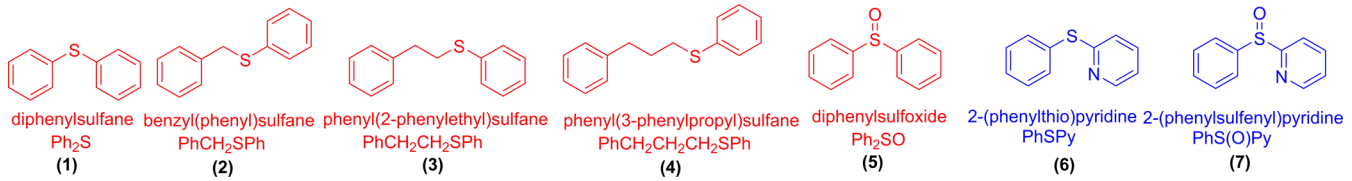


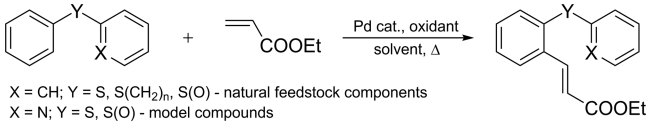
Figure 1. Substrates for C−H bond alkenylation used in the present study.

C−H functionalization with regard to the processing of natural feedstock and practical applications. To the best of our knowledge, selective C−H functionalization in the mixture of model crude oil-derived components has never been shown earlier.

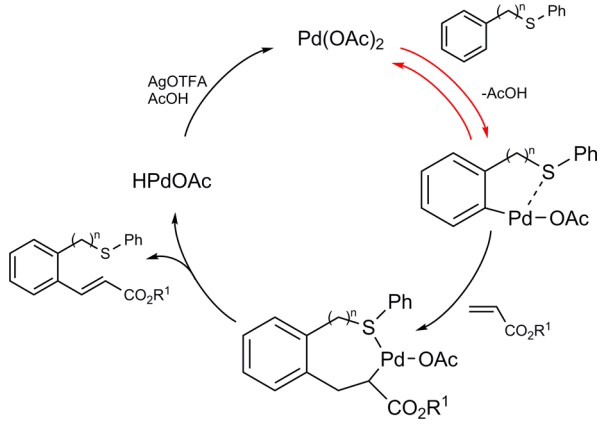
RESULTS AND DISCUSSION

Several possible components and derivatives of the natural feedstock were investigated in a native state without additional directing groups (**1**−**5**), and these substrates were compared with model compounds (**6**, **7**) bearing a pyridyl-directing group (Figure 1).

Scheme 2. Model Alkenylation Reaction Used



Scheme 3. Plausible Reaction Mechanism



The olefination of arenes was conducted using ethyl acrylate as an olefin, and the reaction was performed at 130 °C for 24 h in 1,2-dichloroethane as the solvent (Scheme 2).

Different palladium compounds were studied as catalyst precursors (e.g., $Pd(OAc)_2$, $PdCl_2$, $PdCl_2(MeCN)_2$, $PdCl_2(CyNC)_2$, etc.).[14] The desired alkenylation occurred only with $Pd(OAc)_2$, which was used in the subsequent reactions. Careful selection of the oxidants was carried out to mediate the transformation of interest and simultaneously to avoid the oxidation of the sulfur group. Several oxidants (i.e., $K_2S_2O_8$, $PhI(OAc)_2$, AgOTFA, and oxygen) were examined with each substrate,[14] and a mixture of gaseous oxygen and solid AgOTFA was the most efficient combination. For the individual sulfur substrates shown in Figure 1, product formation was observed for natural feedstock species **2**, **3**, and **4** and for model compounds **6** and **7**, but sulfane **1** and sulfoxide **5** remained unreacted.[14]

For a comprehensive analysis, all of the possible two-component combinations of substrates were examined under similar conditions (equimolar amounts of the two compounds were used as starting materials). A slight excess of the olefin (1.2 equiv) and 2.0 equiv of the oxidant were used to facilitate the transformation of interest. The extent to which the catalyst would render a selective transformation is the most important factor.

Surprisingly, for all of the studied two-component mixtures, only one product was observed with a single component in the mixture subjected to alkenylation. Benzyl(phenyl)sulfane (**2**) was the most reactive among all of the substrates. In the studied mixtures, sulfane **2** was selectively functionalized to afford the respective product in good yield. Phenyl(2-phenylethyl)sulfane (**3**) was the second-most reactive substrate to afford the corresponding alkenylation product in all of the mixtures except when mixed with benzyl(phenyl)sulfane (**2**). A good yield of the corresponding alkenylation product was also observed (61%). Surprisingly, phenyl(3-phenylpropyl)-sulfane (**4**), which contains three CH_2 groups in the chain, was totally inactive. Product formation was not observed for diphenylsulfane (**1**) or diphenylsulfoxide (**5**). For comparative purposes, we utilized 2-(phenylthio)pyridine (**6**) and 2-(phenylsulfinyl)pyridine (**7**), the structural analogs of Ph_2S and Ph_2SO, which contain a pyridine ring instead of a phenyl group. Indeed, both substrates were alkenylated but with lower reactivity compared with benzyl(phenyl)sulfane (**2**) and phenyl(2-phenylethyl)sulfane (**3**).

On the basis of the data acquired, we can estimate the following order of substrates based on their reactivity: benzyl(phenyl)sulfane (**2**) > phenyl(2-phenylethyl)sulfane (**3**) > 2-(phenylsulfinyl)pyridine (**7**) > 2-(phenylthio)pyridine (**6**) > phenyl(3-phenylpropyl)sulfane (**4**), diphenylsulfane (**1**), diphenylsulfoxide (**5**).

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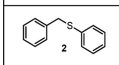
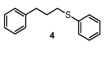
Table 1. Pd-catalyzed C−H Alkenylation in Two-Component Mixtures Containing Sulfur Compounds (See Scheme 2 for Reaction)[a]

Substrates[b]							
		 57	 51	 56	 57	 48	 52
	 57		 61	 56	 58	 49	 59
	 51	 61		 31	 45	 25 / 57[c]	 24/ 57[c]
	 56	 56	 31		 28	 25 / 49[d]	 27 / 50[d]
	 57	 58	 45	 28		NR	NR
	48	49	25 / 57[c]	25 / 49[d]	NR		NR
	52	59	24 / 57[c]	27 / 50[d]	NR	NR	

[a]Conditions: both substrates (0.25 mmol), catalyst $Pd(OAc)_2$ (10 mol %), ethyl acrylate (0.30 mmol; 0.50 mmol for pyridine-containing substrates), and silver trifluoroacetate (AgOTFA; 0.50 mmol) in 5 mL of solvent at 130 °C for 24 h in a closed vial under an oxygen atmosphere; NMR yields are shown in each reaction (NR—no reaction observed); for the studied mixtures, the mono-/diolefination ratio was in the range of 5:1−6:1. [b]Nondiagonal elements of the table correspond to two-component mixtures of the shown starting materials with the structure of the product given in each case (diagonal elements correspond to single-component mixtures, which are described in Table S1 of the Supporting Information). [c]$PhI(OAc)_2$ was used as the oxidant. [d]$K_2S_2O_8$ was used as the oxidant.

For all of the two-component systems, the reaction proceeded exclusively with one component in the mixture, and naturally occurring thioethers **2** and **3** were more reactive than the corresponding thiopyridines or sulfoxides. In addition, with a larger amount of olefin (2.0 equiv), no alkenylation of the second component in the mixture was observed. However, the dialkenylated product from the same substrate was formed.

Inspired by the results for the two-component systems, we evaluated the selectivity of representative multicomponent mixtures that contained several sulfur species as derivatives of a natural feedstock (Table 2).

For the three-component mixture consisting of Ph_2S, Ph_2SO, and $PhCH_2SPh$, the alkenylation occurred exclusively for $PhCH_2SPh$ (entry 1, product yield 45%), as predicted by the established reactivity order. Alkenylation of the three-component mixture consisting of Ph_2S, Ph_2SO, and $Ph(CH_2)_2SPh$ led to the selective alkenylation of $Ph(CH_2)_2SPh$ (entry 2, 52%). For the three-component mixture consisting of Ph_2SO, $PhCH_2SPh$, and $Ph(CH_2)_2SPh$, the alkenylation occurred only for $PhCH_2SPh$ (entry 3, 50%). A similar result was achieved for the mixture consisting of $PhCH_2SPh$, $Ph(CH_2)_2SPh$, and $Ph(CH_2)_3SPh$ (entry 4, 48%) with high selectivity. The addition of pyridyl-containing substrates to the system did not change the alkenylation substrate, which remained $PhCH_2SPh$ (entry 5, 42%). An increase in the number of thioether/sulfoxide components to four and five (entries 6 and 7, respectively) did not affect the selectivity of the alkenylation process, which led to the exclusive alkenylation of $PhCH_2SPh$ (50 and 52% yields, respectively). Therefore, the reaction solely targeted one component of the three-, four-, and five-component systems, and the order of reactivity of the substrates observed for the two-component mixtures was retained in these cases.

To address the scope of the reaction, other olefins (methyl acrylate and *n*-butyl acrylate) were evaluated, and the observed selectivity was retained. Finally, to demonstrate the potential of this reaction for practical application, we performed a 10-fold scaling of the reaction mixtures and observed that the selectivity and the product yields remained unchanged even though a longer reaction time (36 h instead of 24 h) was required. Importantly, the sulfur center was preserved in its native state without oxidation by the oxidant used to mediate the reaction.

The plausible reaction mechanism involves the coordination of the substrate, followed by S-directed C−H activation, alkene insertion, and β-hydrogen elimination (Scheme 3). The difference in the reactivity of the studied substrates can originate from the first step of the catalytic cycle. The substrate with $n = 1$ possesses the most favorable geometry for coordination and subsequent C−H activation. The reaction should be possible for the substrate with $n = 2$, whereas the involvement of the substrate with a longer chain ($n \geq 3$) is unlikely. The proposed mechanistic picture is in agreement with the observed experimental data. Indeed, as a preliminary mechanistic study, the recorded kinetic curves suggested that the favorable binding of the substrates to the catalyst plays a key role in the selective transformation because minimal differences were observed in the reactions involving individual components (Figure S1). A more detailed mechanistic understanding of the reaction involving a mixture of substrates is challenging and will be the subject of future studies.

CONCLUSIONS

To summarize, outstanding substrate selectivity was observed in the C−H alkenylation of organosulfur compounds consisting of crude oil-derived components. Structurally similar components can be distinguished using a selective catalytic transformation. After the incorporation of a functional group (i.e., the CH═CH−COOEt group in the studied case), the separation of the product from the mixture becomes a routine task. By contrast, the separation of the initial mixture of structurally very similar sulfur species into individual com-

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pounds and the destroy/rebuild sequence are extremely cost- and energy-demanding processes.

Crude oil components are the richest natural source of organosulfur compounds with the largest turnover of sulfur species in chemical manufacturing. Therefore, a mixture of naturally occurring sulfur species is a very cheap starting material. If preliminary separation and purification of the starting materials is not required, this approach can change the paradigm of organic compound production. This discovery opens up new opportunities in the field of sustainable organic chemistry with unprecedented cost and energy efficiency.

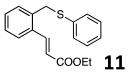
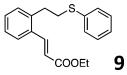
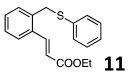
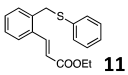
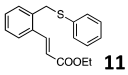
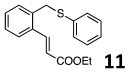
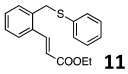
Of course, it should be noted that the present study demonstrates only a general concept using a simple model system. Particularly, the substrate selectivity of C−H functionalization in more complex and randomly varied mixtures of natural crude oils should be studied in more detail. Another important point is to find a suitable and easily available oxidant instead of a stoichiometric amount of silver salt. Several improvements would be required for the development of a catalytic procedure to functionalize natural crude oil samples.

EXPERIMENTAL SECTION

Following is the typical procedure for the alkenylation of a single substrate. The substrate (0.25 mmol), ethyl acrylate (0.30 mmol or 0.50 mmol for pyridine-containing substrates), $Pd(OAc)_2$ (5.6 mg, 10 mol %), and the selected solid oxidant (0.50 mmol, except those with oxygen only) in either DCE or $MeNO_2$ (2 mL) were placed in a 25 mL tube with a screw cap. For all of the reactions except those with oxygen, the test tube was filled with argon and sealed. For reactions with oxygen, oxygen was bubbled through the solution for 2 min, and then the tube was sealed. The reaction vessel was placed in an oil bath and heated to 110 °C for 24 h under vigorous stirring. Then, the reaction mixture was allowed to cool to room temperature and filtered through a pad of celite, which was flushed with several portions of an ethyl acetate/hexane mixture (1:4) until the total volume of the solvent was 25 mL. All of the washes were combined, and the solution was evaporated under reduced pressure at 65 °C. Then, the residue was subjected to flash column chromatography (silica gel, ethyl acetate/hexane = 1:30 − 1:10, v/v) to obtain the desired products. The products were characterized using high-resolution ESI-MS and ^1H and ^{13}C NMR spectroscopy. Also see Table S1 for additional details regarding the experimental conditions.

Following is the typical procedure for the alkenylation of the mixtures. A mixture of the substrates (0.25 mmol of each substrate), ethyl acrylate (0.30 mmol or 0.50 mmol for pyridine-containing substrates), $Pd(OAc)_2$ (5.6 mg, 10 mol %), and AgOTFA (110.5 mg, 0.50 mmol) in DCE (5 mL) was placed in a 25 mL tube with a screw cap. Then, oxygen was bubbled through the solution for 2 min, and the tube was sealed, placed in an oil bath, and stirred at 130 °C for 24 h. The reaction mixture was cooled to room temperature and filtered through a pad of celite, which was flushed with several portions of an ethyl acetate/hexane mixture (1:4) until the total volume of the solvent reached 25 mL. All of the washes were combined, and the solvent was evaporated under reduced pressure at 50 °C. The residue was subjected to flash column chromatography (silica gel, ethyl acetate/hexane = 1:30 − 1:10, v/v) to obtain the desired products. The products were identified using ^1H and ^{13}C NMR and HR-ESI-MS. See comments in Tables 1 and 2 for additional details regarding the experimental conditions.

Table 2. C−H Alkenylation in the Mixtures of Sulfur Substrates (See Scheme 2 for Reaction)[a]

Entry	Multicomponent mixture	Product	Yields, %
1	Ph_2S (**1**) + $PhCH_2SPh$ (**2**) + Ph_2SO (**5**)	 **11**	45 (6:1)
2	Ph_2S (**1**) + $Ph(CH_2)_2Ph$ (**3**) + Ph_2SO (**5**)	 **9**	52 (6:1)
3	$PhCH_2SPh$ (**2**) + $Ph(CH_2)_2SPh$ (**3**) + Ph_2SO (**5**)	 **11**	50 (6:1)
4	$PhCH_2SPh$ (**2**) + $Ph(CH_2)_2SPh$ (**3**) + $Ph(CH_2)_3SPh$ (**4**)	 **11**	48 (6:1)
5	$PhCH_2SPh$ (**2**) + PhSpy (**6**) + PhS(O)py (**7**) Ph_2S (**1**)	 **11**	42 (5:1)
6	+ $PhCH_2SPh$ (**2**) + $Ph(CH_2)_2SPh$ (**3**) + $Ph(CH_2)_3SPh$ (**4**)	 **11**	50 (6:1)
7	Ph_2S (**1**)+ Ph_2SO (**2**) + $PhCH_2SPh$ (**3**) + $Ph(CH_2)_2SPh$ (**4**) + $Ph(CH_2)_3SPh$ (**5**)	 **11**	52 (6:1)

[a]Conditions: each substrate (0.25 mmol), catalyst $Pd(OAc)_2$ (10 mol %), ethyl acrylate (0.30 mmol), and AgOTFA (0.50 mmol) at 130 °C for 24 h in a closed vial under an oxygen atmosphere; NMR yields and mono-/diolefination ratios are shown.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00137.

Materials and measurements, optimization of reaction conditions, NMR and MS spectral data and preliminary kinetic measurements (PDF)

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Notes

The authors declare no competing financial interest.

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(14) See Supporting Information for details and procedures.

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