Palladium-Catalyzed Synthesis of Allylic and Benzylic Sulfides from the Corresponding Dithiocarbonates

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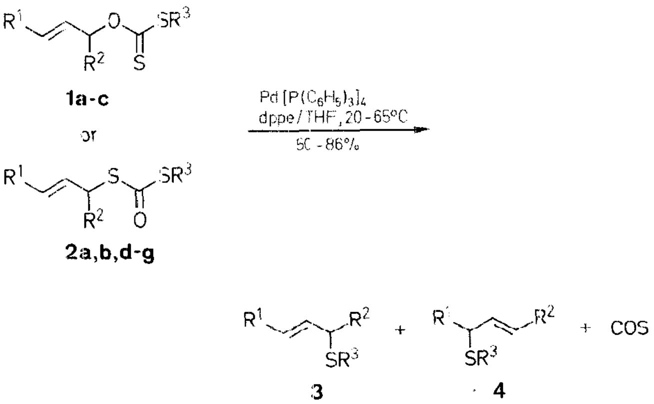
Allylic and benzylic sulfides are prepared from *O*-(2-alkenyl) or *S*-(2-alkenyl) *S*-alkyl and *O*-benzyl *S*-alkyl dithiocarbonates in the presence of palladium(0)-phosphine complex as a catalyst.

Allylic sulfides (2-alkenyl sulfides) are important reagents in organic syntheses.[1] The usual methods for their preparation are based on the reaction of alkyl halides or alcohols with mercaptans.[2] Here, we report a new method for the synthesis of allylic sulfides from allylic dithiocarbonates.

We have found that *O*-(2-alkenyl) or *S*-(2-alkenyl) dithiocarbonates (**1** or **2**, respectively) can be converted to the corresponding sulfides (**3** and/or **4**) under mild conditions in one



dppe = 1,2-bis(diphenylphosphino)ethane

Table 1. 2-Alkenyl Alkyl Sulfides **3** ($R^2 = H$)[a] from *O*-(2-Alkenyl) *S*-Alkyl Dithiocarbonates **1** ($R^2 = H$)

1,3	R^1	R^3	Reaction Conditions	Yield[b] (%)	b.p. (°C)/torr found	b.p. (°C)/torr reported
a	H	$CH_2C_6H_5$	20°C, 8 h	78	70/0.3[c]	121–122/12[10]
b	H	n-C_3H_7	20°C, 10 h	50	136–138	138–140[11]
c	C_6H_5	CH_3	20°C, 20 h	73	100/0.3[c]	142–144/14[12]

[a] All products gave satisfactory MS, IR, and NMR data.

[b] Yield of isolated product.

[c] Bath temperature of short-path distillation.

Table 2. 2-Alkenyl Alkyl Sulfides[a] **3** and **4** from *S*-(2-Alkenyl) *S*-Alkyl Dithiocarbonates **2**

2	R^1	R^2	R^3	Reaction Conditions	Products	Yield[b] (%)	b.p. (°C)/torr		Reported Thermolysis of **2**[7]		
							found	reported	Temp. (°C)	Product	Yield (%)
a	H	H	$CH_2C_6H_5$	45°C, 6 h	**3a** = **4a**	78	70/0.3[c]	121–122°/12[10]			
b	H	H	n-C_3H_7	35°C, 8 h[d]	**3b** = **4b**	54	136–138	138–140[11]			
d	H	CH_3	$CH_2C_6H_5$	50°C, 20 h	**3d** + **4d** (70:30)[e]	79	130/0.5[c]	**3d:** 127/19[13] **4d:** 137–139/18[13]	215–225	**4d**	78
e	CH_3	H	$CH_2C_6H_5$	50°C, 9 h 65°C, 10 h	**3d** + **4d** (75:25)[e] **3d** + **4d** (50:50)[e]	83					
f	H	C_6H_5	CH_3	45°C, 4 h	**4f**	67	100/0.3[c]	142–144/14[12]	200	**4f**	85
g	H	C_6H_5	n-C_3H_7	45°C, 10 h	**4g**	67	100/0.3[c]	not given[14]			

[a, b, c] See Table 1.

[d] Ether is used as solvent instead of tetrahydrofuron.

[e] Ratio determined by ^{1}H-NMR analysis.

Table 3. Benzyl Alkyl Sulfides[a] **6** from O-Benzyl *S*-Alkyl Dithiocarbonates **5**

5,6	R^1	R^2	Reaction Conditions	Yield[b] (%)	b.p. (°C)/torr found	b.p. (°C)/torr reported
a	H	$CH_2CH{=}CH_2$	65°C, 7 h	32[f]	70/0.3[c]	121–122/12[10]
b	H	CH_3	65°C, 4 h	65	96/21	52–54/1.8[15]
c	H	C_2H_5	65°C, 7 h	92	104/23	220–223/atmos.[16]
d	H	n-C_3H_7	65°C, 21 h	77	120/20	112/14[17]
e	H	$CH_2COOC_2H_5$	65°C, 7 h	54	256/atmos.	134–136/1.7[18]
f	H	CH_2CN	45°C, 11 h	68	252/atmos.	94–99/0.1–0.2[19]
g	3-CH_3	CH_3	40°C, 13 h	81	87–88/6	not given[20]

[a, b, c] See Table 1.

[f] Diallyl sulfide and dibenzyl sulfide were obtained as by-products.

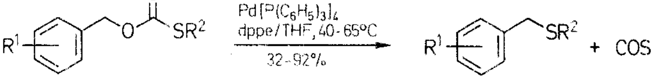
step in the presence of catalytic amounts of tetrakis[triphenylphosphine]-palladium and 1,2-bis[diphenylphosphino]-ethane (dppe).

Carbon oxide sulfide (COS) can coordinate with palladium(0) to produce a palladium dithiocarbonate complex.[3] The above mentioned reaction did not occur in the presence of triphenylphosphine instead of dppe; the solution became red immediately and formed a precipitate which had the same IR absorptions as those reported for the Pd-dithiocarbonate complex, implying that the catalyst may be deactivated by the coordination with carbon oxide sulfide. Thus, dppe is necessary for this reaction since it has stronger coordinating ability with the metal and thus prevents the coordination of carbon oxide sulfide with palladium.

The sulfide formation can be explained by the following mechanism. The first step involves the oxidative addition of the allylic dithiocarbonate to Pd(0); then, evolution of COS affords the π-allylic palladium complex, which is similar to those formed in the reaction of allylic carbonates.[4,5] Finally, the reaction of the thiolate ion with the π-allylic palladium complex produces the allylic sulfide and regenerates the Pd(0) catalyst.

The conversion of *O*-(2-alkenyl) dithiocarbonates (xanthates, **1**) to sulfides has been reported to proceed under basic phase-transfer conditions,[6] but many by-products are also formed. A recent paper describes the formation of allylic sulfides by thermolysis of corresponding xanthates but the reaction temperature is much higher.[7] Thus, the catalytic reaction reported here offers a more convenient and useful method to prepare allylic sulfides.

Benzyl alkyl sulfides (**6**) may also be prepared in one step from the corresponding dithiocarbonates (**5**) under similar conditions.



5a-g **6a-g**

Other analogous benzylic compounds, e.g., benzyl carbonate, *S*-benzyl *O*-alkyl thiocarbonates, and *O*-benzyl *S*-alkyl thiocarbonates failed to react under the same conditions. Details and mechanism of this reaction with benzylic compounds are currently investigated in our laboratory.

2-Alkenyl Alkyl Sulfides (3, 4); General Procedure:

The *O*- or *S*-(2-alkenyl) *S*-alkyl dithiocarbonate[8] (**1**, or **2**; 1.0 mmol) is added to a stirred solution of tetrakis[triphenylphosphine]-palladium[9] (58 mg, 0.05 mmol) and 1,2-bis[diphenylphosphino]-ethane (dppe;

Table 4. Spectral Data of Compounds **3**, **4** and **6**

Compound	MS[a] m/e (M^+)	IR (neat)[b] ν (cm^{-1})	^{1}H-NMR (CCl_4)[c] δ (ppm)
3a = **4a** = **6a**	164	1635, 910	2.98 (d, 2H, $J = 7$ Hz, $=\mathrm{CHC\underline{H}_2}$); 2.62 (s, 2H, $\mathrm{C\underline{H}_2C_6H_5}$); 4.84–5.30 (m, 2H, $=\mathrm{C\underline{H}_2}$); 5.40–6.20 (m, 1H, $\mathrm{H_2C{=}C\underline{H}{-}}$); 7.28 (s, 5$\mathrm{H_{arom}}$)
3b = **4b**	116	1650, 880	0.90 (t, 3H, $J = 7$ Hz, $\mathrm{CH_2C\underline{H}_3}$); 1.15–1.73 (m, 2H, $\mathrm{-CH_2C\underline{H}_2CH_3}$); 2.30 (t, 2H, $J = 7$ Hz, $\mathrm{-C\underline{H}_2CH_2-}$); 2.96 (d, 2H, $\mathrm{=CHC\underline{H}_2-}$); 4.70–5.16 (m, 2H, $\mathrm{\underline{H}_2C{=}CH-}$); 5.30–6.10 (m, 1H, $\mathrm{H_2C{=}C\underline{H}-}$)
3c	164	1680, 1600, 965	1.93 (s, 3H, $\mathrm{-SC\underline{H}_3}$); 3.08 (d, 2H, $J = 6$ Hz, $\mathrm{=CHC\underline{H}_2S-}$); 5.73–6.47 (m, 2H, $\mathrm{-C\underline{H}{=}C\underline{H}-}$); 7.17 (s, 5$\mathrm{H_{arom}}$)
3d + **4d**	178	1650, 970	1.21 (d, $J = 4$ Hz, $\mathrm{-SCH(C\underline{H}_3)-}$; 1.65 (d, $J = 6$ Hz, $\mathrm{C\underline{H}_3CH{=}}$); 2.70–3.20 (m, $\mathrm{=CHC\underline{H}_2S-}$ and $\mathrm{-SC\underline{H}(CH_3)-}$; 3.48 (s, 2H, $\mathrm{C\underline{H}_2C_6H_5}$); 4.80–5.6 (m, $\mathrm{-C\underline{H}{=}C\underline{H}-}$); 7.15 (s, 5$\mathrm{H_{arom}}$)
4g	192	1640, 960	0.94 (t, 3H, $J = 7$ Hz, $\mathrm{CH_2C\underline{H}_3}$); 1.20–1.90 (m, 2H, $\mathrm{-CH_2C\underline{H}_2CH_3}$); 2.38 (t, 2H, $J = 7$ Hz, $\mathrm{-SC\underline{H}_2CH_2-}$); 3.15 (d, 2H, $J = 6$ Hz. $\mathrm{=CHC\underline{H}_2S-}$); 5.76–6.50 (m, 2H, $\mathrm{-C\underline{H}{=}C\underline{H}-}$); 7.22 (s, 5$\mathrm{H_{arom}}$)
6b	138	1605, 772	1.82 (s, 3H, $\mathrm{SC\underline{H}_3}$); 3.48 (s, 2H, $\mathrm{SC\underline{H}_2C_6H_5}$); 7.15 (s, 5$\mathrm{H_{arom}}$)
6c	152	1605, 772	1.10 (t, 3H, $J = 7$ Hz $\mathrm{CH_2C\underline{H}_3}$); 2.25 (q, 2H, $J = 7$ Hz, $\mathrm{C\underline{H}_2CH_3}$); 3.53 (s, 2H, $\mathrm{C\underline{H}_2C_6H_5}$); 7.14 (s, 5$\mathrm{H_{arom}}$)
6d	166	1610, 780	0.94 (t, 3H, $J = 7$ Hz, $\mathrm{CH_2C\underline{H}_3}$); 1.24–1.98 (m, 2H, $\mathrm{C\underline{H}_2CH_3}$); 2.32 (t, 2H, $J = 7$ Hz, $\mathrm{-SC\underline{H}_2CH_2-}$); 3.62 (s, 2H, $\mathrm{C\underline{H}_2C_6H_5}$); 7.26 (s, 5$\mathrm{H_{arom}}$)
6e	210	1735 ($C{=}O$); 1600, 775	1.26 (t, 3H, $J = 6$ Hz, $\mathrm{OCH_2C\underline{H}_3}$); 2.88 (s, 2H, $\mathrm{C\underline{H}_2C_6H_5}$); 3.26 (s, 2H, $\mathrm{-SC\underline{H}_2CO_2-}$); 4.10 (q, 2H, $J = 6$ Hz, $\mathrm{OC\underline{H}_2CH_3}$); 7.28 (s, 5$\mathrm{H_{arom}}$)
6f	163	2250 (–CN); 1600	2.96 (s, 2H, $\mathrm{C\underline{H}_2C_6H_5}$); 4.88 (s, 2H, $\mathrm{-SC\underline{H}_2CN}$); 7.30 (s, 5$\mathrm{H_{arom}}$)
6g	152	1610, 790	1.90 (s, 3H, $\mathrm{Ar{-}C\underline{H}_3}$); 2.35 (s, 3H, $\mathrm{SC\underline{H}_3}$); 3.56 (s, 2H, $\mathrm{-C\underline{H}_2S-}$); 6.80–7.30 (br., 4$\mathrm{H_{arom}}$)

[a] The mass spectra were recorded with a Finnigan 4021 spectrometer.
[b] The IR spectra were recorded with a Specord 75-IR spectrometer.
[c] The ^{1}H-NMR spectra were recorded with a 60 MHz Varian EM 360 spectrometer.

40 mg, 0.1 mol) in tetrahydrofuran (5 ml) under purified nitrogen. The solution is heated with stirring and the reaction is monitored by TLC (disappearance of dithiocarbonate) and by the cease of evolution of carbon oxide sulfide. The mixture is then passed through a short column of silica gel to remove the catalyst. The sulfide was isolated by distillation or column chromatography.

Benzyl Alkyl Sulfides (6); General Procedure:

The *O*-benzyl *S*-alkyl dithiocarbonate[8] (**5**; 1.0 mmol) is added to a stirred solution of tetrakis[triphenylphosphine]-palladium[9] (58 mg, 0.05 mmol) and 1,2-bis[diphenylphosphino]-ethane (dppe; 40 mg, 0.1 mmol) in tetrahydrofuran (5 ml). The solution is heated and stirred and the reaction is monitored by TLC (disappearance of the starting material **5**) and also by the cease of evolution of carbon oxide sulfide. The mixture is then evacuated to remove the solvent. The product **6** is isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

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