Efficient Route to  $\gamma,\delta$ -Unsaturated Carbonyl Compounds from Allyl Sulfides and  $\alpha-Diazocarbonyls$  Using a Rhodium Catalyst

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Functionalized  $\gamma, \delta$ -unsaturated carbonyl compounds are efficiently prepared from allyl sulfides and  $\alpha$ -diazo carbonyl compounds by catalysis of rhodium (II) acetate.

The catalytic effectiveness of rhodium (II) compounds for spontaneous ylide generation and [2,3]-sigmatropic rearrangement in reaction of diazo compounds with allylic hetero compounds have widely recognized in recent years.<sup>1)</sup> In relation to our ongoing project, we report here a highly effective synthesis of some functionalized  $\gamma$ ,  $\delta$ -unsaturated carbonyl compounds (<u>4</u>) from the allyl phenyl sulfides (<u>1</u>) by spontaneous ylide generation and [2,3]-sigmatropic rearrangement using rhodium (II) acetate as catalyst.

The reaction can be carried out by refluxing the sulfides<sup>2)</sup> (<u>1</u>) and a small excess amount of the diazo carbonyl compounds<sup>3)</sup> (<u>2</u>) in toluene in the presence of a catalytic amount of rhodium (II) acetate<sup>4)</sup> for several minutes to give rise to the  $\gamma, \delta$ -unsaturated compounds (<u>4</u>) in excellent yields. Although neither the ylide intermediates (<u>3</u>) nor cyclopropane derivatives are detected, it is believable that carbenoid intermediates generated by catalytic decomposition of the diazo compounds (<u>2</u>) react with the sulfides (<u>1</u>) to give ylides (<u>3</u>) which subsequently rearrange to the products (<u>4</u>) via the [2,3]-sigmatropic pathway<sup>1</sup>) (Scheme 1). The compounds obtained by the present procedure have a potential for the synthesis of a variety of compounds due to their high functionality.

A typical procedure is as follows: A mixture of sulfide <u>1b</u> (270 mg, 1.0 mmol) and diazo compound <u>2a</u> (223 mg, 1.2 mmol) in toluene (10 ml) is stirred with rhodium diacetate (9 mg, 0.02 mmol) at room temperature. After having dissolved the catalyst (ca. 10 min),<sup>5)</sup> the purple solution is refluxed for 15 min to complete the reaction. After removal of the solvent, the residue is chromatographed (SiO<sub>2</sub>) to give the product<sup>6)</sup> <u>4d</u> (384 mg, 90%).



Scheme 1.

Table 1. Reaction of Allyl Sulfides with $\alpha$ -Diazocarbonyls									
Entry	Subst	trate	$Product(\underline{4})$	Yield/%	Entry Substrate		cate	$Product(\underline{4})$	Yield/%
1	<u>1a</u>	<u>2a</u>	$\underbrace{\overset{\text{SPh}}{\overbrace{\text{CO}_2^{\text{Et}}}}}_{\underline{4a}}$	84.3	7	<u>1c</u>	<u>2a</u>	<u>4d</u>	83.4
2	<u>1a</u>	<u>2b</u>	4b SPh0	33.9 (62.8 <sup>a)</sup> )	8	<u>1c</u>	<u>2b</u>	<u>4e</u>	61.1
3	<u>1a</u>	<u>2c</u>	$\underbrace{\underbrace{\operatorname{SPh}}_{O=P(OEt)_2}^{SPh}}_{4c}$	81.1	9	<u>1c</u>	<u>2c</u>	<u>4f</u>	100
4	<u>1b</u>	<u>2a</u>	$ \begin{array}{c}                                     $	89.7	10	<u>1d</u>	<u>2a</u>	H SPhO	82.7
5	<u>1b</u>	<u>2b</u>	BnO <u>4e</u>	63.4	11	<u>1d</u>	<u>2b</u>	$\frac{4g}{H}$	<sup>2</sup> 26.6 (62.9 <sup>a)</sup> )
6	<u>1b</u>	<u>2c</u>	H SPh CO <sub>2</sub> Et BnO O=P(OEt) <sub>2</sub> <u>4f</u>	90.4	12	<u>1d</u>	<u>2c</u>	$H \qquad SPh \\ CO_2Et \\ CO_2Et \\ O = P (OEt)_2 \\ \underline{4i}$	80.3

a) 2.4 Equivalents of <u>2b</u> are used.

References

- 1) M. P. Doyle, Acc. Chem. Res., 19, 348 (1986) and references cited therein.
- 2) Prepared in good yield from each corresponding alcohol precursor applying Hata's conditions: see, I. Nakagawa, K. Aki, and T. Hata, J. Chem. Soc., Perkin Trans. 1, 1983, 1315.
- Trans. 1, <u>1983</u>, 1315.
  3) Prepared in good yield by treating the carbonyl compounds with <u>p</u>-toluene-sulfonyl azide in the presence of triethylamine for <u>2a</u> and <u>2b</u> or sodium hydride for <u>2c</u>.
- 4) Freshly prepared from rhodium (II) chloride: see, P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, J. Chem. Soc., A, <u>1970</u>, 3322.
- 5) No reaction takes place at this stage.
- 6) All new compounds obtained exhibit satisfactory spectral (IR, <sup>1</sup>H-NMR, MS) and analytical (combustion or high resolution mass) data.

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