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Efficient Route to γ,δ-Unsaturated Carbonyl Compounds from Allyl Sulfides and α-Diazocarbonyls Using a Rhodium Catalyst

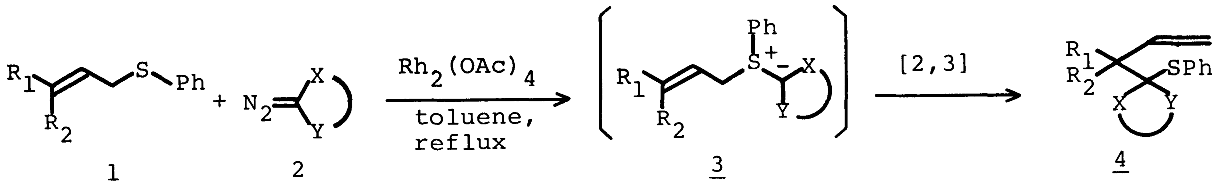
Seiichi TAKANO,* Shun'ichi TOMITA, Michiyasu TAKAHASHI, and Kunio OGASAWARA
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

Functionalized γ,δ-unsaturated carbonyl compounds are efficiently prepared from allyl sulfides and α-diazo carbonyl compounds by catalysis of rhodium (II) acetate.

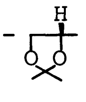
The catalytic effectiveness of rhodium (II) compounds for spontaneous ylide generation and [2,3]-sigmatropic rearrangement in reaction of diazo compounds with allylic hetero compounds have widely recognized in recent years.[1)] In relation to our ongoing project, we report here a highly effective synthesis of some functionalized γ,δ-unsaturated carbonyl compounds (4) from the allyl phenyl sulfides (1) 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[2)] (1) and a small excess amount of the diazo carbonyl compounds[3)] (2) in toluene in the presence of a catalytic amount of rhodium (II) acetate[4)] for several minutes to give rise to the γ,δ-unsaturated compounds (4) in excellent yields. Although neither the ylide intermediates (3) nor cyclopropane derivatives are detected, it is believable that carbenoid intermediates generated by catalytic decomposition of the diazo compounds (2) react with the sulfides (1) to give ylides (3) which subsequently rearrange to the products (4) via the [2,3]-sigmatropic pathway[1)] (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 1b (270 mg, 1.0 mmol) and diazo compound 2a (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),[5)] the purple solution is refluxed for 15 min to complete the reaction. After removal of the solvent, the residue is chromatographed (SiO_2) to give the product[6)] 4d (384 mg, 90%).



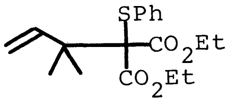
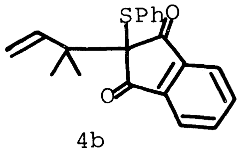
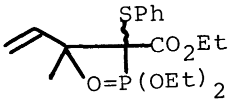
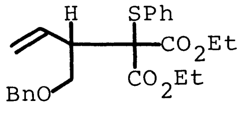
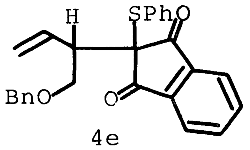
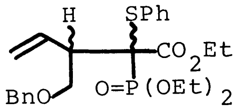
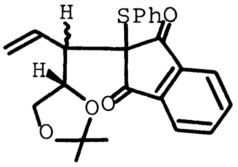
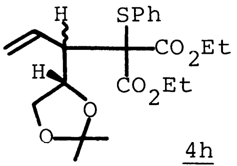
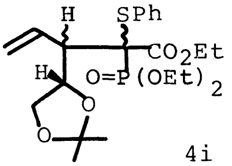
1 2 3 4

1a : $R_1=R_2=Me$ 1b : $R_1=H$, $R_2=CH_2OBn$ 1c : $R_1=CH_2OBn$, $R_2=H$ 1d : $R_1=(S)-$ 

2a : $X=Y=CO_2Et$ 2b : X,Y=(o)-phthaloyl 2c : $X=CO_2Et$, $Y=\overset{O}{\overset{\|}{P}}(OEt)_2$

Scheme 1.

Table 1. Reaction of Allyl Sulfides with α-Diazocarbonyls

Entry	Substrate		Product(4)	Yield/%
1	1a	2a	 4a	84.3
2	1a	2b	 4b	33.9 (62.8[a])
3	1a	2c	 4c	81.1
4	1b	2a	 4d	89.7
5	1b	2b	 4e	63.4
6	1b	2c	 4f	90.4
7	1c	2a	4d	83.4
8	1c	2b	4e	61.1
9	1c	2c	4f	100
10	1d	2a	 4g	82.7
11	1d	2b	 4h	26.6 (62.9[a])
12	1d	2c	 4i	80.3

a) 2.4 Equivalents of 2b 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.

3) Prepared in good yield by treating the carbonyl compounds with p-toluenesulfonyl azide in the presence of triethylamine for 2a and 2b or sodium hydride for 2c.

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, 1970, 3322.

5) No reaction takes place at this stage.

6) All new compounds obtained exhibit satisfactory spectral (IR, ^{1}H-NMR, MS) and analytical (combustion or high resolution mass) data.

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