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A New Propargylic Rearrangement of Acetylenic Alcohols by P_4S_{10}. A New Preparative Method for Monothio-α-diketone

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Treatment of acetylenic alcohols with phosphorus pentasulfide P_4S_{10} at room temperature gave thioketones. Similarly, treatment of acetylenic alcohol having a carbonyl group on its acetylenic carbon gave monothio-α-diketone. It was clarified that four sulfur atoms of P_4S_{10} are involved in the reaction.

Propargylic rearrangement is a useful synthetic method for a wide variety of organic compounds from acetylenic alcohols which are readily available by addition of acetylenes to carbonyl compounds.1) However, no propargylic rearrangement which is concerned with introduction of sulfur atom has been known so far. We now report the first example of the propargylic rearrangement of acetylenic alcohols by phosphorus pentasulfide P_4S_{10} which gives thioketone derivatives. When this method is applied to an acetylenic alcohol which has a carbonyl on its acetylenic carbon, monothio-α-diketone was obtained.

General procedure of the reaction is as follows: A solution of acetylenic alcohol and an equimolar amount of P_4S_{10} in toluene was stirred at room temperature and the toluene solution was washed with 10% aqueous NaOH and water, and dried over Na_2SO_4. The crude crystals obtained by evaporation of toluene were recrystallized from benzene to give pure thioketone. For example, treatment of **1a** and **1b** with P_4S_{10} for 6 h as above gave **3a** (23% yield, mp 175-177 °C, δ(=CH) 6.5 ppm, λ_{max} 280 nm (ε 7800))2) and **3b** (45% yield, mp 78-80 °C, δ(=CH) 6.6 ppm, λ_{max} 294 nm (ε 8200)), respectively. Acetylenic alcohols (**4**) having carbonyl substituent are much more reactive toward P_4S_{10}, and **4a**-**f** gave **5a**-**f** easily (Table 1).

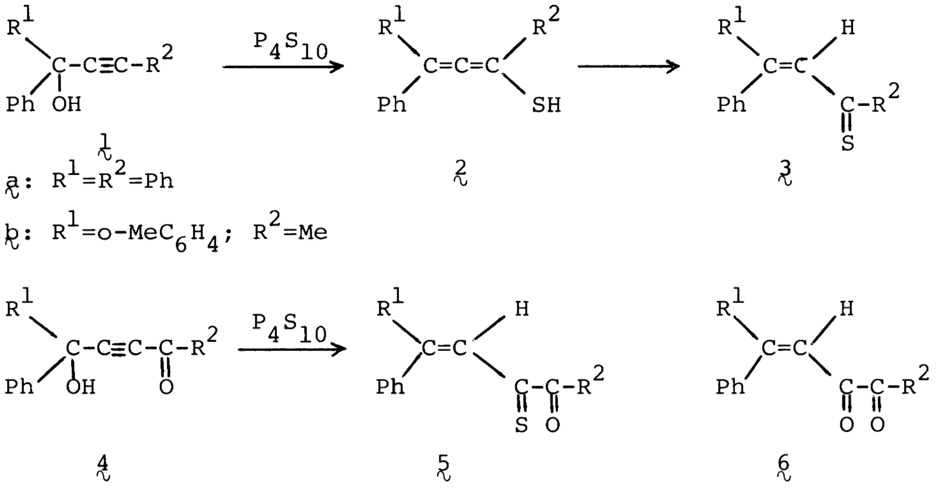
Structure of **3** and **5** was also elucidated by mass spectral data. For example, **5a** showed the following peaks, *m/e* 328 (M^+, 93%), 223 (M^+-PhCO, 100%), and 105

(PhCO, 99%). Furthermore, $KMnO_4$ oxidation of **5** gave the same α-diketone (**6**) as that obtained by a Meyer-Shuster rearrangement of **4**. Of course, no reaction of **6** with P_4S_{10} occurred at room temperature. However, geometry around the carbon-carbon double bond of **3b**, **5c**, and **5d** was not determined.

When a molar ratio of P_4S_{10} to **4a** is diminished in the reaction from 1:1 to 1:2, 1:4, and 1:8, the yield of **5a** changed from 85% to 87%, 80%, and 30%, respectively. These results show that four sulfur atoms of P_4S_{10} are available to the reaction, and the structure of P_4S_{10} (Fig. 1) suggests that the sulfur atoms of four P=S bonds are involved in the reaction. However, it is not clear whether the propargylic rearrangement (for example, **1** to **2**) occurs through a concerted pathway or stepwise one via acetylenic thiol intermediate.

Table 1. Preparation of **5** by reaction of **4** with P_4S_{10} at room temperature in toluene

5	R^1	R^2	Reaction time/h	Yield %	Mp θ_m/°C	δ(=CH) (ppm)	λ_{max} nm	(εx10^{-2})
a	Ph	COPh	2	85	181-182	6.8	391	(264)
b	Ph	p-COC_6H_4Me	2	78	164-165	6.8	396	(248)
c	o-Cl-C_6H_4	COPh	2	31	162-163	6.7	393	(260)
d	iBu	COPh	4	40	72-75	6.7	387	(237)
e	Ph	COiPr	5	31	oil	7.2	352	(76)
f	Ph	COMe	5	42	oil	6.2	350	(59)



a: $R^1=R^2=Ph$

b: $R^1=o\text{-}MeC_6H_4$; $R^2=Me$

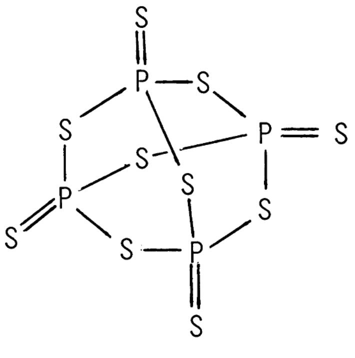


Fig. 1. Structure of P_4S_{10}.

References

1) J. H. wotiz, "Chemistry of Acetylenes," ed by H. G. Viehe, Marcel Dekker, New York (1969), p. 365.

2) All NMR and UV spectra were measured in $CDCl_3$ and $CHCl_3$, respectively.

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