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PHOTODIMERIZATION OF PRENYL MERCAPTAN

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Allylic mercaptans have been known to be relatively unstable compounds and to be polymerized to the polysulfide thiols1),2). Moreover, Obata and Tanaka reported that prenyl mercaptan(γ,γ-dimethyl allyl mercaptan)(I) was the major component of the sun light flavor of beer3). So it appeared interesting to examine the photochemical behavior of prenyl mercaptan. In this paper, we wish to report that I is photodimerized to cis- and trans-2,5-diisopropyl-1,4-dithian(IIIc and IIIt) in good yield.

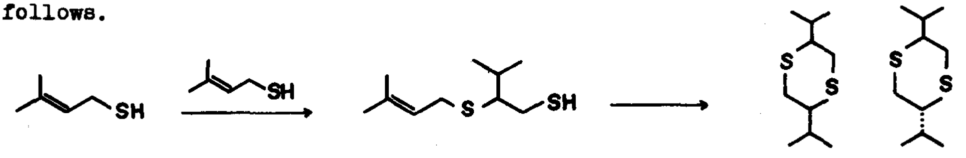
U.v. irradiation of a n-hexane solution of I with a 30 W low pressure mercury lamp at a distance of 5 cm under nitrogen led to quantitative conversion of I into III.

trans-2,5-Diisopropyl-1,4-dithian(IIIt): Colorless needles, mp 71.8-72.2° (Ethanol). The mass spectrum showed the parent peak at m/e 204, and the relative intensity of M, M+1 and M+2 peaks (100, 14.00 and 10.87 respectively) supported the formula $C_{10}H_{20}S_2$. In the ir spectrum, the absorption bands at 1130, 1170, 1370 and 1395 cm^{-1}(isopropyl groups) were observed. The pmr spectrum(60 MHz, CCl_4) exhibited signals at τ 7.17-7.36(m, 6H, dithian ring protons), τ 7.94-8.57(m, 2H, $-C\underline{H}(CH_3)_2$) and τ 9.03(d, 12H, $-CH(C\underline{H}_3)_2$, J=6.9Hz). The pmr data suggest that two isopropyl groups are equivalent to the dithian ring, and therefore are trans.

cis-2,5-Diisopropyl-1,4-dithian(IIIc): Liquid. The mass and ir spectra supported the structure of III. The pmr spectrum showed the methyl protons of isopropyl groups at τ 9.03(d, 6H, J=6.9Hz) and τ 8.96(d, 6H, J=6.9Hz).

These data show that two isopropyl groups are nonequivalent and therefore are *cis* configuration.

In addition, sulfide thiol(II)[4] was isolated from the reaction mixtures (Table 1). Therefore, I is dimerized to II and II changes to IIIc and IIIt by means of intramolecularcyclization. And this reaction route seems to be as follows.



(I) (II) (IIIc) (IIIt)

The details will be reported in the near future with the conformation of these dithians.

Table 1. Photodimerizations of Prenyl Mercaptan(I)(1.5 g) in *n*-Hexane(3.5 ml) at Room Temperature. (In a quartz tube)

Reaction time (hr)	Yield (%)	Products (percent by glc analyses) II	IIIc	IIIt	Unknowns
1	28	23	15	58	4
2	49	13	17	66	4
7	89	3	19	72	6
11	97	trace	20	74	6

References and Footnote

1) J. v. Braun and T. Plate, *Ber.*, *67*, 281(1934).

2) A. A. Oswald, USP 3,503,940 (1970).

3) Y. Obata and H. Tanaka, *Agr. Biol. Chem.*(Tokyo), *29*, 104 (1965).

4) The physical constants of II: mass(m/e); 204(M$^+$), 170(M-H$_2$S). ir(cm^{-1}); 830(δ_{CH}), 2560(ν_{SH}). pmr(60 MHz, CCl$_4$, τ); 9.01(d, 6H, J=6.0Hz), 8.28 and 8.35(two singlets, 6H), 7.95-8.68(m, 2H), 7.34(t, 2H, J=7.7Hz), 6.88 (d, 2H, J=7.9Hz), 6.75-7.18(m, 1H), 4.85(t, 1H, J=7.9Hz).