Communications to the Editor

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PHOTOREACTION OF N-2-ALKENYLTHIOPHTHALIMIDES: 1,4-DITHIANE FORMATION BY INTRA- AND INTERMOLECULAR TWO-FOLD PHOTOREACTIONS AND THE X-RAY ANALYSIS OF THE DITHIANES[1)]

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Upon irradiation, N-2-alkenylthiophthalimides (**8** and **9**) effectively gave 1,4-dithianes as a pair of stereoisomers. The structures of the products, **10b-i** and **10b-ii**, are confirmed on the basis of their X-ray analyses. Plausible reaction pathways are discussed.

KEYWORDS — thiophthalimide; alkenyl group; 1,4-dithiane; X-ray analysis; photoreaction

Dithiane formation is one of characteristic features of the photochemistry of thiocarbonyl systems (1) such as thiones[2)] and thioimides.[3)] To formulate a general pattern of this reaction, we have recently reached the following hypothesis: A non-thiyl biradical (2) is the common primary intermediate of photoaddition of certain olefins to thiocarbonyl compounds (1). In the case of thiones, 2 is trapped by a highly reactive thione such as thiobenzophenone through the **T** (thione) pathway, forming a second biradical (3) which ultimately affords

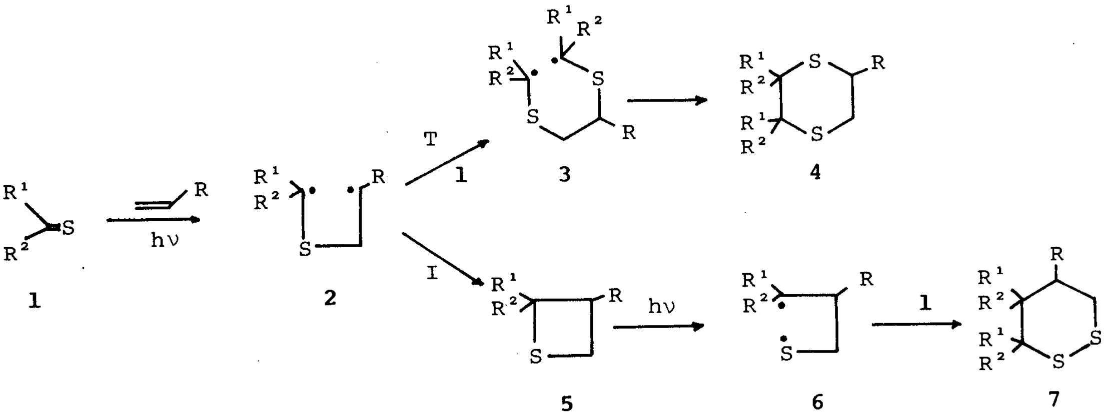
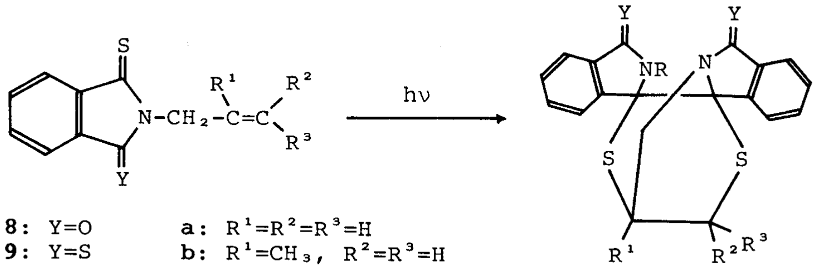


Chart 1

1,4-dithiane (**4**). But with thioimides, **2** immediately couples to imide-thietanes (**5**), through pathway I (imide), followed by subsequent photolysis forming a thiyl biradical (**6**). This biradical takes up the second molecule of thioimide **1** to afford 1,2-dithianes (**7**)3) (Chart 1).

Recently we found that on irradiation, N-alkenylthiosuccinimides form multicyclic strained imide-thietanes.4) However, it turned out that the aromatic counterparts take a very different reaction course. In this paper we report a new two-fold photoreaction of N-alkenylthiophthalimides (**8** and **9**) involving a relay of the intra- and intermolecular reaction sequence to form not 1,2-, but 1,4-dithianes.

Photolyses of **8** and **9** in benzene were carried out with a 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere for 1-2 h at room temperature. In all cases, only a pair of stereoisomers (**10** and **11**) in approximately a 1 : 1 ratio were obtained in good total yields. The results are listed in Table I (Chart 2).



8: Y=O
9: Y=S

a: $R^1=R^2=R^3=H$
b: $R^1=CH_3$, $R^2=R^3=H$
c: $R^1=H$, $R^2=R^3=CH_3$

10: Y=O
11: Y=S

$R=-CH_2CR^1=CR^2R^3$

Chart 2

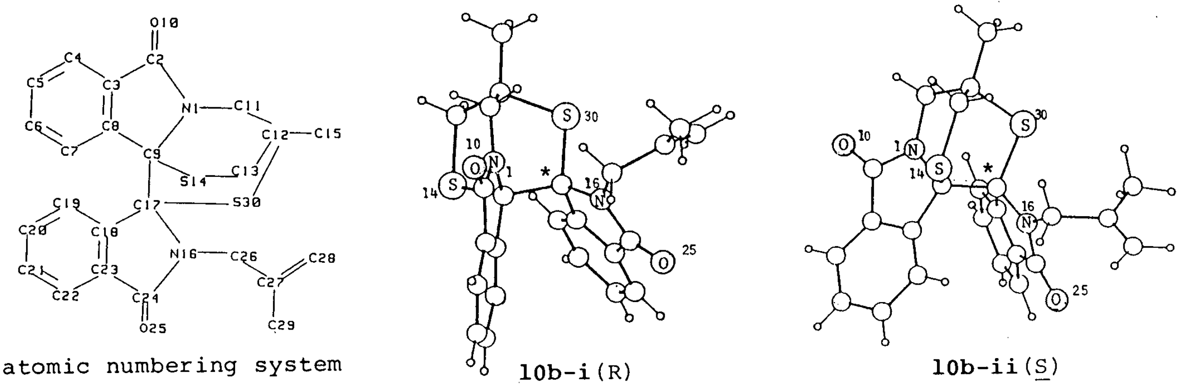
Table I. Photoproducts for **8**,**9**

Substrate	Irradiation time (h)	Yield % (mp °C)			
8a	1	**10a-i**	38(200-201)	**10a-ii**	35(206-207)
8b	1	**10b-i**1)	41(248.5-249)	**10b-ii**2)	33(244-246)
8c	2	**10c-i**	29(218-219.5)	**10c-ii**	28(221-222)
9a	1	**11a-i**	34(200-201))	**11a-ii**	41(206-207)
9b	1	**11b-i**	37(240-241.5)	**11b-ii**	38(244-245)
9c	2	**11c-i**	42(198-199)	**11c-ii**	29(202-204)

1) The configuration of carbon*-17 is R on the basis of the X-ray analysis.
2) (carbon*-17: S).

The mass spectra of **10** and **11** indicated that the products consist of two molecules of the substrates (**8** and **9**). The ^{13}C-NMR spectra showed the presence of two lactams (thiolactams) and one alkenyl group. This suggests that the reaction took place among a thiocarbonyl group, one alkenyl group, and a thiocarbonyl of a second molecule.

To confirm the stereochemical structures of **10** and **11**, one pair of products (**10b-i** and **10b-ii**) was analyzed by X-ray. In Fig. 1 the molecular structures of **10b-i** (R with respect to the spiro carbon*-17) and **10b-ii** (S) which incorporate the 1,4-dithiane rings are shown.[5)] The structures of the other products (10 and 11) were assigned on the basis of their analogy with the ^{1}H- and ^{13}C-NMR spectra of **10b-i** and **10b-ii** as reference compounds.



atomic numbering system used in the X-ray analysis

10b-i (R)

10b-ii (S)

Fig. 1. Molecular Structures of **10b-i** and **10b-ii**

Thus, the complete structural elucidation for **10b-i** and **10b-ii** gave not only structural confirmation for the other products but also an important clue to solve the mechanism of the pathways of the 1,4-dithiane formation in this system. As shown in Chart 3, the reaction is presumably initiated by C-S bond formation to generate an intermediate biradical (**12**), corresponding to **2** in Chart 1. The biradical (**12**) immediately traps **8b**, as if it were thiones, through a T pathway (pathway A) to form the final products (**10b-i** and **10b-ii**). This is in competition with pathway C (I in Chart 1) in which **12** couples to thietane **13**. Pathway A is compatible with that[2)] proposed by Ohno et al. and de Mayo et al. (path T in Chart 1). Pathways B and C seem less important since none of thietanes (**13**) and 1,3-dithianes (**10b-iii**) were detected in the reaction mixture.[6)] Although the nature of the excited states involved is unknown, presumably the key intermediate

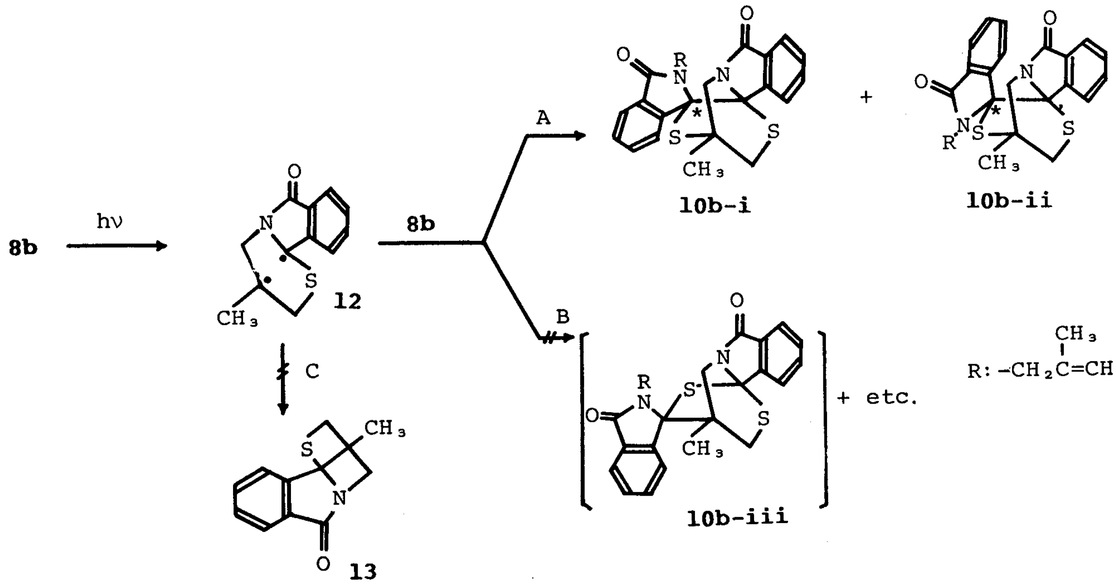


Chart 3

is the initially generated biradical (12), which preferentially traps a second molecule of **8b** intermolecularly to form dithianes (10b). This is due, at least in part, to its relatively long life-time. The restricted planarity of 12 caused by a benzene ring may be another factor preventing the formation of multicyclic thietane. This 1,4-dithiane formation, interpreted by a special intra- and intermolecular radical mechanism, seems to be a very rare event in the thioimide dithiane family.

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5) Crystal data for **10b-i** —— $C_{24}H_{22}N_2O_2S_2$, M_r=434.58, monoclinic, a=16.264(2), b=17.100(3), c=16.246(2)Å, β=107.743(9)°, U=4303(1)Å^3, Z=8, Dm=1.341gcm^{-3}, space group $C_{2/c}$. Crystal data for **10b-ii** —— $C_{24}H_{22}N_2O_2S_2$, M_r=434.58, triclinic, a=9.747(1), b=12.261(2), c=9.267(1)Å, α=105.393(6), β=95.745(7), γ=95.510(7)°, U=1053.7(2)Å^3, Z=2, Dm=1.370gcm^{-3}, space group $P_{\bar{1}}$.

6) In the photoreactions of thiones 1,3-dithianes could be isolated in the experiments at low temperature. The reason why the 1,3-dithianes (**10b-iii** etc.) are not formed is uncertain. The latter, if any, will easily undergo thermal decomposition to form the thietane.[2b]

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