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PHOTOCHEMICAL REACTIONS OF 1,2-DITHIOLE-3-THIONES AND RELATED COMPOUNDS WITH OLEFINS

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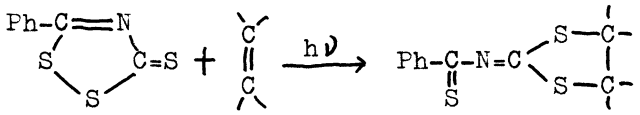
Photochemical reactions of 5-phenyl- and 4,5-diphenyl-3H-1,2-dithiole-3-thiones with olefins gave 2-thiobenzoylmethylene-1,3-dithiolanes. Ethylenetrithiocarbonate, 2H-1,3-dithiole-2-thione or 3H-1,2-dithiole-3-one did not react with cyclohexene under the same condition, but the first compound gave 7,8-tetramethylene-1,4,6,9-tetrathia-spiro[4.4]nonane by irradiation with low-pressure mercury lamp.

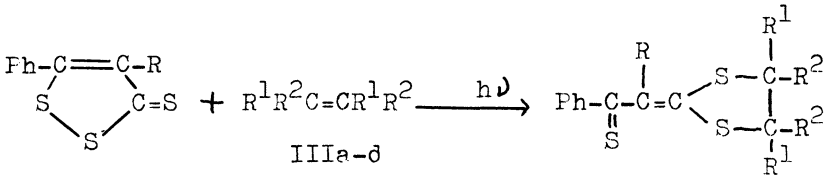
It has been found that 5-phenyl-3H-1,2-dithiole-3-thione reacts thermally with active acetylenes to give 2-thiobenzoylmethylene-2H-1,3-dithioles[1], but there is no report on reactions with olefins.

We reported previously that photochemical reactions of 5-phenyl-3H-1,2,4-dithiazole-3-thione with olefins gave 2-thiobenzoylimino-1,3-dithiolanes.[2]



In this report, we would like to report that 3H-1,2-dithiole-3-thiones undergo photochemical reaction in the presence of olefins in a similar manner.

Irradiation of the thione (I[3] or II[4]) (5 mmol) and olefin (III) (7 ml) in benzene (70 ml) with a high-pressure mercury lamp (100 W) under nitrogen at room temperature for 2-6 hr gave 2-thiobenzoylmethylene-1,3-dithiolanes (IV or V) as green crystals (see Table). The reaction mixture was indicated to contain only one reaction product by means of TLC.



I: R=H

II: R=Ph

IIIa-d

a: R^1=H, R^2R^2=-$(CH_2)_3$-

b: R^1=H, R^2R^2=-$(CH_2)_4$-

c: R^1=H, R^2R^2=-$(CH_2)_6$-

d: R^1=R^2=Me

IVa-d: R=H

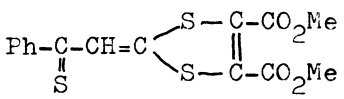
Va-d: R=Ph

Table. Yields and physical properties of 2-thiobenzoylmethylene-1,3-dithiolanes (IV and V)

	Yield(%)	Mp(°C)	Color
IVa R^1=H, R^2R^2=-$(CH_2)_3$-	59.6	122-123	dark green
IVb R^1=H, R^2R^2=-$(CH_2)_4$-	60.4	89-91	deep green
IVc R^1=H, R^2R^2=-$(CH_2)_6$-	72.6	99-100	yellow-green
IVd R^1=R^2=Me	32.1*	126-127	dark green
Va R^1=H, R^2R^2=-$(CH_2)_3$-	65.6	153-154	green
Vb R^1=H, R^2R^2=-$(CH_2)_4$-	70.9	183-184	yellow-green
Vc R^1=H, R^2R^2=-$(CH_2)_6$-	85.0	162-163	green
Vd R^1=R^2=Me	30.8*	155-156	deep green

* The thione (I or II) did not decompose completely under the reaction condition.

The structure of the products (IV or V) was established by their analytical[5] and spectral data; e. g., for IVb, NMR ($CDCl_3$): δ 1.9 (m, 8H), 4.2 (m, 2H), 7.35 (m, 3H), 7.75 (m, 2H), and 7.85 (s, 1H); λ_{max}^{EtOH} 259 (ε 1.42 X 10^4), 330 (1.35 X 10^4), 430 (2.07 X 10^4) and 625 nm (2.66 X 10^3); MS: m/e 292 (M^+); IR: 1160 (C=S) and 615 cm^{-1} (C-S). These UV spectra are very similar to that of an analogous compound (VI).[1]



VI

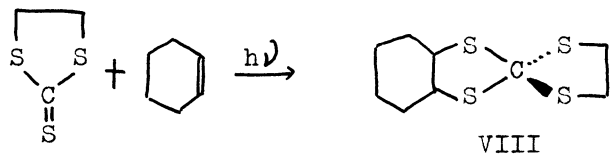
The stereochemistry at 4- and 5-positions in the reaction products was not determined.

These reactions did not occur in the absence of light. The thione (I or II) itself was scarcely decomposed under the same condition.

In the connection with the above results, photochemical reaction of cyclic trithiocarbonates or 3H-1,2-dithiole-3-ones with cyclohexene was tried expecting analogous reactions. However, starting materials were recovered upon irradiation of ethylenetrithiocarbonate (VII),[6] 4,5-diphenyl-2H-1,3-dithiole-2-thione[7] or 5-phenyl-3H-1,2-dithiole-3-one[3] in benzene-cyclohexene with a high-pressure mercury lamp (100 W) under nitrogen at room temperature for 20-26 hr.

On the contrary, irradiation of VII (32 mmol) and cyclohexene (51.8 mmol) in dichloromethane (120 ml) with a low-pressure mercury lamp (160 W) for 48 hr gave pale yellow crystals (VIII) (0.536 g, 29% based on VII consumed), mp 117.5-120°C (from methanol), together with unchanged VII (51%), unknown product and dark green tarry material.

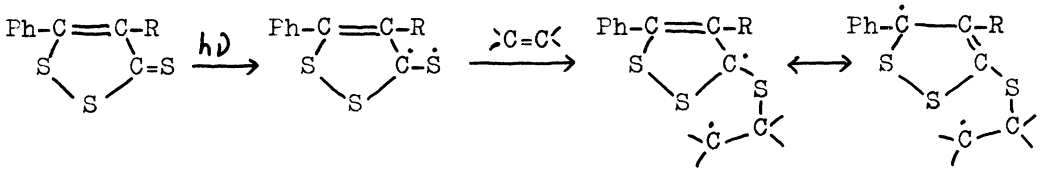
The compound (VIII), $C_9H_{14}S_4$, was assigned as 7,8-tetramethylene-1,4,6,9-tetrathia-spiro[4.4]nonane by the elemental analysis and the spectral data.



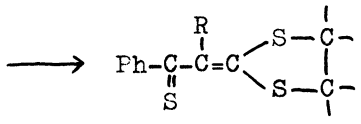
VII VIII

The formation mechanism of VIII is not clear yet.

From the above facts, the group -S-S-C(=S)- is considered to be necessary for the photochemical reactions with olefins. Therefore, a plausible mechanism for photochemical reaction with olefins is considered to be as follows.



IX



The driving force in these reactions is attributable to formation of conjugate C=S bond from an intermediate biradical (IX), in which the S-S bond

undergoes an induced decomposition intramolecularly.

Further works are in progress.

References

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