Photochemical Reactions of 5-Phenyl-1,2,4-dithiazole-3-thione with Olefins: a New Route to 1,3-Dithiolan Rings

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Summary Photochemical reactions of 5-phenyl-1,2,4-dithiazole-3-thione with olefins lead to the formation of 1,3-cyclo-addition products, derivatives of 2-thiobenzoylimino-1,3-dithiole.

ALTHOUGH five-membered-ring heterocycles with the –S–C(=S)– group have been reported[1–3] to undergo cycloaddition–ring-opening reactions with acetylenes having electron-withdrawing substituents, there have been no reports on the reactions with olefins.

We present here the first example of a photochemical reaction of a 1,2,4-dithiazole-3-thione with olefins. This 1,3-cycloaddition is a new route to 1,3-dithiolan derivatives.

Irradiation of the thione (I) (4 mmol)[2a] and olefin (II) (7 ml) in benzene with a high-pressure mercury lamp

(100 W) under nitrogen for 5 h, followed by chromatographic separation (silica gel) gave the 1,3-dithiolans (III) as coloured crystals (see Table).

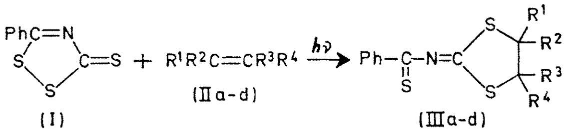
TABLE

Yields and properties of 2-thiobenzoylimino-1,3-dithiolans (III)

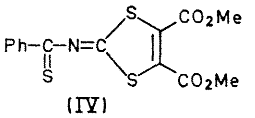
	Yields (%)	Products (III) M.p. (°C)	Colour
(IIa), $R^1 = R^4 = H$, $R^2R^3 = \cdot[CH_2]_3\cdot$ ..	64	66—67	Purple
(IIb), $R^1 = R^4 = H$, $R^2R^3 = \cdot[CH_2]_4\cdot$ ..	62(75)*	75—77	Green
(IIc), $R^1 = R^4 = H$, $R^2R^3 = \cdot[CH_2]_6\cdot$ ..	60	119—120	Green
(IId), $R^1 = R^2 = R^3 = R^4 = Me$	40	104—105	Reddish purple

* In 25% (v/v) cyclohexene solution.

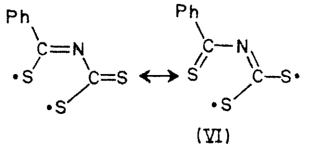
The structure of products (III) was established by their analytical and spectral data; *e.g.* (IIIb), τ (CCl_4) 1·5—1·7 (2H, m), 2·3—2·6 (3H, m), 5·8—6·2 (2H, br), and 7·8—8·6 (8H, br), λ_{max} (CH_2Cl_2) 248 (ε 11,500), 324 (20,200), 378 (9140), and 560 nm (99), *m/e* 293 (M^+) and 135 (base), ν_{max} (KBr disc) 1195 cm^{-1} (C=S). The u.v. spectrum, which is very similar to that of the analogous compound (IV)[2a] [λ_{max} 254 (ε 18,350), 338 (15,600), and 406 nm (13,400)], strongly supports the proposed structure (III).



(I) (IIa-d) (IIIa-d)



(IV)



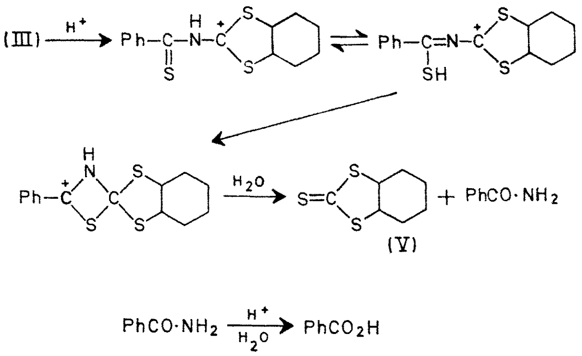
(VI)

These reactions did not occur in the absence of light.

Irradiation with a low-pressure mercury lamp (160 W, 10 h) gave similar results, though the yield was lower owing to partial decomposition of the product (III). Thus, after irradiation for 20 h, almost half the thiolan (IIIb) had decomposed to form the dithiazolethione (I) (7%).

Acid hydrolysis of (IIIb) in dichloromethane–ethanol afforded *cis*-cyclohexylenetrithiocarbonate (V) (m.p. 101—103°) and benzoic acid. The structural assignment of (V) was based on its analytical and spectral data, and its chemical behaviour: τ ($CDCl_3$) 5·58 (2H, m) and 7·7—8·7 (8H, br),[4] λ_{max} (n-hexane) 316 nm (ε 14,100),[5] *m/e* 190 (M^+, base), ν_{max} (KBr disc) 1090s and 1053vs cm^{-1} (C=S).[6] The trithiocarbonate (V) was found to be different from the reported *trans*-derivative[7] in m.p., retention time in g.l.c., and behaviour in the reaction with triethyl phosphite; the trithiocarbonate obtained here produced cyclohexene, while the *trans*-derivative has been reported to give a tetrasubstituted olefin, 4,4′,5,5′-bistetramethylene-$\Delta^{2,2'}$-bi-1,3-dithiolan.[8]

These facts are indicative of *cis*-fusion between the cyclohexane and dithiole rings in (IIIb). The unexpected formation of (V) is explicable by a pathway involving intramolecular attack of a highly nucleophilic thiol group on a carbonium ion centre (see Scheme).



SCHEME

Olefins with electron-withdrawing substituents, such as maleic anhydride and dimethyl maleate, yielded no addition products. Therefore, we concluded that the reactive species adding to olefins might not be 1,3-dipolar, but free radicals. We consider that the mechanism *via* a diradical (VI) formed by S–S fission is most plausible, though the possibility can not be excluded at the present stage that an excited *n*π* state of (I) is involved.

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