

Photochemical Reactions of 1,2,4-Dithiazole-3-thione and 1,2-Dithiole-3-thione with Olefins

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Photoreactions of 5-phenyl-1,2,4-dithiazole-3-thione (1) and of 5-phenyl- (2) and 4,5-diphenyldithiole-3-thione (3) with olefins lead to 2-thiobenzoylimino- (5), 2-thiobenzoylmethylene- (6), and 2-(α -thiobenzoylbenzylidene)-1,3-dithiolans (7), respectively, in good yields. The reactions are nonstereospecific with regard to the adding olefin, both *cis*- and *trans*-but-2-ene affording a mixture of two isomeric dithiolans (10) and (11) upon reaction with (2). The dithiazolethione (1) photochemically decomposes in the absence of olefin to give imidazole derivatives (13) and (14) while the dithiolethiones (2) and (3) are stable. A mechanism involving a diradical (20) is proposed.

THE photochemistry of the thiocarbonyl group has been of considerable interest recently,¹⁻⁶ but most reports have concentrated on the photochemical behaviour of thioketones.⁷

As a continuation of our work on the reactivity of

¹ A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, 1969, **91**, 5038, and references therein; A. Ohno, T. Koizumi, and Y. Ohnishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 2511; N. Kito and A. Ohno, *Chem. Comm.*, 1971, 1338; A. Ohno and N. Kito, *Internat. J. Sulfur Chem., A*, 1971, **1**, 26.

² K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, 1968, **33**, 1240.

³ H. J. T. Bos, H. Schinkel, and Th. C. M. Wijsman, *Tetrahedron Letters*, 1971, 3905.

⁴ T. S. Cantrell, *J. Org. Chem.*, 1974, **39**, 853.

⁵ D. R. Kemp, A. H. Lawrence, C. C. Liao, R. O. Loufty, P. de Mayo, A. A. Nicholson, and S. Pazyc, XXIIIrd International Congress of Pure and Applied Chemistry, 1971, vol. 1, p. 367; D. S. L. Blackwell, P. de Mayo, and R. Suan, *Tetrahedron Letters*, 1974, **91**, and preceding papers of this series.

⁶ H. Gotthardt, *Chem. Ber.*, 1972, **105**, 2008; *Tetrahedron Letters*, 1973, 1221.

⁷ *E.g.*, U. Schmidt and K. H. Kabitzke, *Angew. Chem.*, 1964, **76**, 687; U. Schmidt, K. H. Kabitzke, I. Boie, and C. Osterroht, *Chem. Ber.*, 1965, **98**, 3819; J. L. Fourrey, P. Jouin, and J. Moron, *Tetrahedron Letters*, 1973, 3229; A. Ohno, T. Koizumi, and Y. Akazaki, *Bull. Chem. Soc. Japan*, 1974, **47**, 319.

sulphur-containing heterocycles with olefins,⁸ we investigated the photochemistry of 1,2,4-dithiazole- and 1,2-dithiole-3-thiones. These thiones, as well as other five-membered heterocycles containing the -S-C(=S)-unit, are known to undergo cycloaddition-ring-opening reactions with active acetylenes,⁹ but there have been no reports on such reactions with olefins.¹⁰ We have

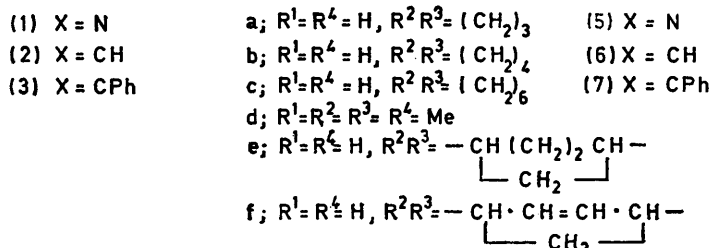
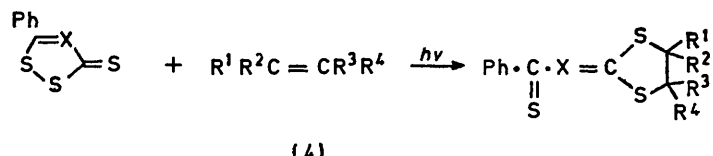
⁸ R. Okazaki, K. Okawa, S. Wajiki, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 3167.

⁹ (a) C. Portail and J. Vialle, *Bull. Soc. chim. France*, 1966, 3187; D. Noel and J. Vialle, *ibid.*, 1967, 2239; H. Davy, M. Demuyunck, D. Paquer, A. Rouessac, and J. Vialle, *ibid.*, 1968, 2057; (b) H. Berlinger, D. Bender, J. Falkenberg, and R. Wiedenmann, *Chem. Ber.*, 1968, **101**, 1428; H. Berlinger, J. Kilger, and R. Wiedenmann, *Tetrahedron Letters*, 1968, 1185; (c) D. B. J. Easton, D. Leaver, and T. J. Rawlings, *J.C.S. Perkin I*, 1972, 41; (d) M. Ahmed, J. M. Buchshriber, and D. M. McKinnon, *Canad. J. Chem.*, 1970, **48**, 1991; D. M. McKinnon and J. M. Buchshriber, *ibid.*, 1971, **49**, 3299; G. E. Bachers, D. M. McKinnon, and J. M. Buchshriber, *ibid.*, 1972, **50**, 2568; M. S. Chauhan, M. E. Hassan, and D. M. McKinnon, *ibid.*, 1974, **52**, 1738; (e) M. Stavaux, *Bull. Soc. chim. France*, 1971, 4426; (f) B. R. O'Connor and F. N. Jones, *J. Org. Chem.*, 1970, **35**, 2002.

¹⁰ However, see G. Hervieu, P. Rioult, and J. Vialle, *Bull. Soc. chim. France*, 1971, 4375, 4380; A. Rouessac and J. Vialle, *ibid.*, 1968, 2054.

reported in a preliminary communication that these cyclic thiones react photochemically with olefins.¹¹ The present paper describes detailed accounts of these photoreactions as well as the photochemistry of related compounds.

Photoreactions of 5-Phenyl-1,2,4-dithiazole-3-thione (1) and 5-Phenyl- (2) and 4,5-Diphenyl-1,2-dithiole-3-thione (3) with Olefins.—The thiones (1)—(3) reacted photochemically with the olefins (4) to give 2-thiobenzoylimino- (5), 2-thiobenzoylmethylene- (6), and 2-(α -thiobenzoylbenzylidene)-1,3-dithiolans (7) in good yields, respectively. Irradiation was carried out in benzene



containing an excess of olefin with Pyrex-filtered light from a high pressure mercury lamp for 2—5 h under

TABLE I

Yields and properties of 2-thiobenzoylimino- (5), 2-thiobenzoylmethylene- (6), and 2-(α -thiobenzoylbenzylidene)-1,3-dithiolan (7)

Product	Yield (%)	M.p. (°C)	Colour	Recrystallization solvent *
(5a)	64	66—67	Purple	E
(5b)	62	75—77	Green	C
(5c)	60	119—120	Green	C
(5d)	40	104—105	Reddish purple	C
(6a)	60	122—123	Dark green	B2
(6b)	60	89—91	Deep green	H
(6c)	73	99—100	Yellowish green	B2
(6d)	32	126—127	Dark green	P
(6e)	86	156—157	Dark green	B2
(6f)	78	269—270	Dark green	iB
(7a)	66	153—154	Green	iP
(7b)	71	183—184	Yellowish green	iP
(7c)	85	162—163	Green	iB
(7d)	31	155—156	Deep green	P
(7e)	89	188—189	Dark green	B2
(7f)	78	194—195	Dark green	B2

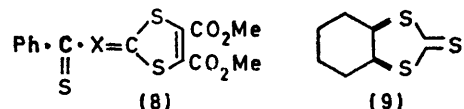
* E, ether; C, carbon tetrachloride; B2, butan-2-ol; H, n-hexane; P, petroleum; iB, isobutyl alcohol; iP, isopropyl alcohol. † In 25% (v/v) cyclohexene solution (see Experimental section).

nitrogen. Generally, the reaction proceeded faster with (2) and (3) than with (1). The results are summarized

¹¹ (a) R. Okazaki, K. Okawa, and N. Inamoto, *Chem. Comm.*, 1971, 843; (b) R. Okazaki, F. Ishii, K. Ozawa, and N. Inamoto, *Chem. Letters*, 1972, 9.

in Table I. The structure of the products (5)—(7) was established by their analytical and spectral data (see Experimental section); the similarity of the u.v. spectra of (5) and (6) to the related system (8) strongly suggests the proposed structure [(8; X = N), λ_{max} (dioxan) 254 (ϵ 18,350), 338 (15,600), and 406 nm (13,400); (8; X = CH), λ_{max} (dioxan) 267 (ϵ 17,300), 340 (11,500), and 468 nm (18,400)].^{9b} Further support for structure (5) was obtained from its hydrolysis products. Acidic hydrolysis of (5b) in dichloromethane-ethanol gave *cis*-1,2-cyclohexylene trithiocarbonate (9), m.p. 101—103° (27%), and benzoic acid (30%) together with some

sulphur. The mechanism of formation of (9) has already been discussed.^{11a} The trithiocarbonate obtained here differed from the reported *trans*-derivative¹² in m.p. (169°), retention time in g.l.c., and behaviour in the reaction with triethyl phosphite; (9) yielded



cyclohexene, while the *trans*-isomer has been reported to give 8,8'-bi-(7,9-dithiabicyclo[4.3.0]nonan-8-ylidene).¹³ Isolation of (9) is indicative of *cis*-fusion between the cyclohexene and the dithiole ring in (5b).

T.l.c. of the reaction mixture indicates that the dithiolan (6) or (7) is the sole product in the reactions of (2) or (3), respectively, whereas an unidentified red oil is also formed besides (5) in each reaction of (1). This oil contains both aromatic and aliphatic systems suggesting that it is the product of a reaction between (1) and (4).

The use of dichloromethane in place of benzene as solvent slightly decreased the reaction rate as well as the yield [50% for (5b)]. Irradiation of the thione (1) with olefin (4b) in dichloromethane using 254 nm light gave virtually the same results, although the yield was somewhat lower. This decrease in yield is partly due to

¹² C. C. J. Culvenor, W. Davies, and K. M. Pausacker, *J. Chem. Soc.*, 1946, 1050.

¹³ E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934.

the lability of the product (5) under the reaction conditions; (5) in dichloromethane, upon irradiation (20 h) with a low pressure mercury arc in a separate experiment, decomposes 50% to give (1) (7%).

The reactions do not occur in the absence of light; even prolonged heating of the thiones (1)—(3) with cyclohexene in benzene resulted in recovery of the starting material.

Photoreaction of (2) with *cis*- or *trans*-but-2-ene was performed with the intention of determining the stereospecificity of the reactions (see Tables 2 and 3). Concurrent formation of *cis*- and *trans*-products (10) and

TABLE 2
Photoreactions of the thione (2) with *cis*- and *trans*-but-2-ene

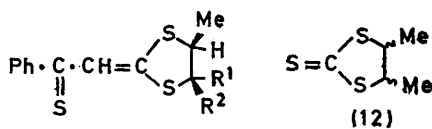
Olefin	(10) (%)	(11) (%)	Total yield (%)	Recovered olefins (%)	
				<i>cis</i>	<i>trans</i>
<i>cis</i> -But-2-ene	50	50	50	98.2	1.8
<i>trans</i> -But-2-ene	17	83	98	<0.5	>99.5

TABLE 3
Chemical shifts (δ) of the dithiolans (10)—(12)

Dithiolan	Methyl protons	Methylene protons
(10) *	1.45	3.90
(11) *	1.54	3.63
$\Delta\delta(t-c)$	0.09	-0.27
<i>cis</i> -(12) †	1.52	4.38
<i>trans</i> -(12) †	1.62	4.11
$\Delta\delta(t-c)$	0.10	-0.27

* In deuteriochloroform. † In carbon tetrachloride, see ref. 14.

(11) from either isomeric butene indicates nonstereospecificity of the reaction. No isomerization is observed in the recovered olefin for reaction with *trans*-but-2-ene, but *cis*-but-2-ene is isomerized to a minor extent. The stereochemistry of the reaction products was determined from n.m.r. data on the basis that the reported data for 4,5-dimethyl-1,3-dithiolane-2-thione (12) are also applicable in the present case; in (12), the methyl signals in *cis*-isomer and the methine signals in the *trans*-isomer appear at higher field (see Table 3).¹⁴



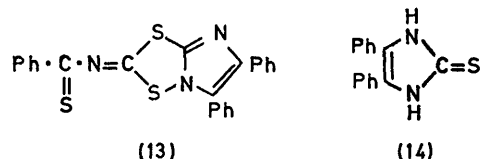
(10) $R^1 = H$, $R^2 = Me$

(11) $R^1 = Me$, $R^2 = H$

Photoreaction of the Thiones (1)—(3) in the Absence of Olefins.—Although the thiones (2) and (3) appear to be stable under the photolytic conditions, the dithiazolethione (1) in benzene decomposed to give (13) and (14) on irradiation under nitrogen. Compound (13) exists as unstable purple crystals which decompose gradually on heating, showing no clear melting point. The elemental analysis and the mass spectrum (M^+ 429) indicate the molecular formula $C_{23}H_{15}N_3S_3$, and the u.v. spectrum

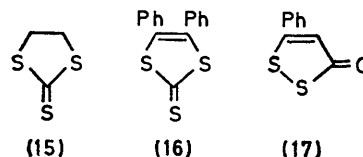
¹⁴ C. G. Overberger and A. Drucker, *J. Org. Chem.*, 1964, 29, 360.

[λ_{max} (CH_2Cl_2) 263 (ϵ 54,100), 319 (22,000), 369 (13,100), and 510 nm (4370)] strongly suggests the presence of a $PhC(=S)N=CS-S-$ group because of the similarity to that of (5b) [λ_{max} 248 (ϵ 11,500), 324 (20,200), 378 (9140), and 560 nm (99)]. The mechanism of formation of (13) and (14) is not clear, although (14) is presumably

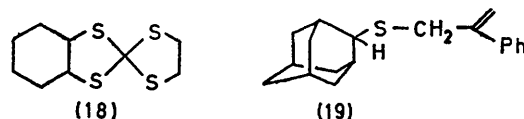


formed by the decomposition of (13) during the isolation procedure. The photolysis of (1) in benzene in the presence of oxygen gives sulphur, (14), and benzamide (13%).

Other Photoreactions.—The photoreactions of the related compounds (15)—(17) were carried out in the hope of developing and determining the structural requirements of the aforementioned photocycloaddition-ring-opening reactions. No appreciable change was



observed upon irradiation of compounds (15)—(17) in benzene-cyclohexene with Pyrex-filtered light for 20—26 h. Irradiation of (15) with a low pressure mercury lamp in dichloromethane-cyclohexene, however, gave pale yellow crystals (18) [29% based on (15) consumed].



No addition product was produced on irradiation of (1) in benzene in the presence of maleic anhydride, dimethyl maleate, or *cis*-dichloroethylene.

DISCUSSION

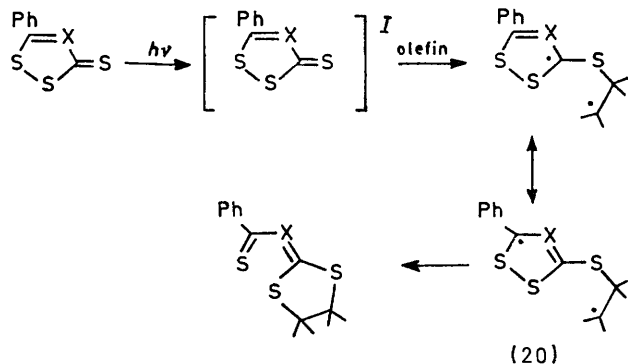
Thiobenzophenone has been reported to undergo ready photochemical addition to several types of olefins to give 1,4-dithian or thietan depending on the nature of substituents on the olefins.^{1-4,15} The reactions of the thiones (1)—(3) with alicyclic and aliphatic olefins studied here do not correspond with that of thiobenzophenone or of adamantanethione, which has been reported to afford (19) along with thietan in photoreaction with α -methylstyrene.¹⁶

Although the complex electronic spectra of the thiones (1)—(3) preclude a detailed study of the reaction mechanism at present, analogy with thiobenzophenone photochemistry suggests the following mechanism,

¹⁵ See also P. de Mayo and H. Shizuka, *Mol. Photochem.*, 1973, 5, 339; *J. Amer. Chem. Soc.*, 1973, 95, 3942.

¹⁶ C. C. Liao and P. de Mayo, *Chem. Comm.*, 1971, 1525.

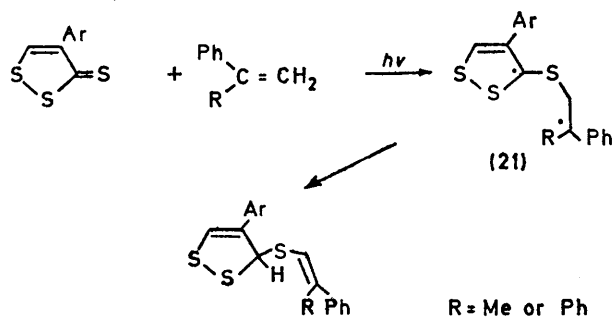
involving a composite biradical (20) formed from the reaction of an excited thione (presumably an $n-\pi^*$ triplet) with an olefin and its subsequent intramolecular induced decomposition of the S-S bond. This reaction



scheme is in keeping with the observations that (i) no addition product is formed in the presence of oxygen, (ii) no addition product is afforded with olefins having electron-withdrawing groups, suggesting the intermediacy of an electrophilic species similar to a thiyl radical, and (iii) the photoaddition is nonstereospecific.

The different *cis:trans* ratios in the products from the isomeric but-2-enes (50:50 for the *cis*-olefin and 17:83 for the *trans*-olefin) clearly indicate that the intramolecular, induced decomposition of the S-S bond by the intermediate radical is fast enough to compete with the C-C bond rotation. In this connection the slow reaction of 2,3-dimethylbut-2-ene with all the thiones studied is illustrative. In this case, since the attacking species is tertiary, and hence stable and space-demanding, this induced decomposition is considered to be less favourable.

Of further interest is the fact that very little or no isomerization is observed in the recovered olefins, implying that nearly all the olefins, once trapped by the thione, lead to the product without reverting to the starting material. This is in accord with the relatively high quantum yield of this reaction ($\Phi = 0.27$ at 434 nm in benzene).¹⁷



In connection with the reaction mechanism, the recent report on 4-aryl-1,2-dithiole-3-thione by de Mayo *et al.*¹⁸

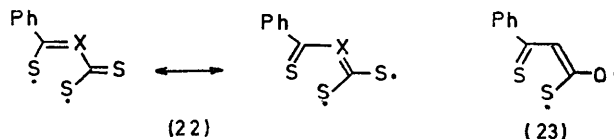
† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

¹⁷ F. Ishii, unpublished results.

¹⁸ P. de Mayo and H. Y. Ng, *Tetrahedron Letters*, 1973, 1561.

is of interest, as it invokes a similar biradical (21). The difference between our and their reaction products may be attributable to the formation of a more stable conjugated thioketone in the former and the less favourable intramolecular induced decomposition in the latter where the attacking radical is more stable and space-demanding.

Finally, the occurrence of biradical (22) as an intermediate in these reactions, which would be expected from the cleavage of the photolytically vulnerable S-S bond, is considered to be unlikely, because 1,2-dithiol-3-one (17), which should generate a similar biradical (23) by S-S bond rupture, did not react with cyclohexene under identical reaction conditions.



EXPERIMENTAL

U.v. spectra were recorded on a Hitachi ESP-3 spectrophotometer. I.r. spectra were taken for KBr discs with a Hitachi EPI-G2 spectrometer. N.m.r. spectra were obtained in carbon tetrachloride or deuteriochloroform solutions at 60 MHz with a Hitachi R-20B or R-24 spectrometer (tetramethylsilane as internal standard). Mass spectra were measured with a Hitachi RMU-6 spectrometer (beam energy 70 eV). G.l.c. analyses were performed with a Hitachi K23 gas chromatograph. Photoreactions were carried out using a high (Rikosha, 100 W) or a low pressure mercury lamp (Rikosha, 160 W); with the former lamp a Pyrex filter was used. All reactions were performed under nitrogen unless otherwise noted. Silica gel was used for column chromatography.

General Procedure for Photoreactions.—The thione (1),¹⁹ (2),²⁰ or (3)²¹ (4–5 mmol) dissolved in a mixture of benzene (70 ml) and the olefin (7 ml) was irradiated with a high pressure mercury lamp for 2–5 h at 15–20°. After evaporation of benzene and excess of olefin the reaction mixture was either chromatographed with carbon tetrachloride–benzene as eluant [in the case of (1)] or recrystallized from an appropriate solvent [in the case of (2) or (3); see Table I] to give the 1,3-dithiolans (5), (6), or (7) as highly coloured crystals. The spectral and analytical data for compounds (5b)–(7b), which are typical, are given below, and the data for the remainder of compounds (5)–(7) are listed in Supplementary Publication No. SUP 21195 (6 pp.): † (5b) (Found: C, 57.1; H, 5.0; N, 4.8; S, 32.6. $C_{14}H_{14}NS_3$ requires C, 57.3; H, 5.1; N, 4.8; S, 32.8%), δ 1.67br (4H, s), 1.93br (4H, s), 3.97 (2H, m), 7.50 (3H, m), and 8.33 (2H, m); ν_{max} 1195 cm^{-1} ; λ_{max} 232 ($\epsilon \times 10^{-3}$ 11.4), 248inf (11.1), 320 (16.6), 370inf (7.55), and 565 nm (0.085); m/e 293 (M^+ , trace), 212 (43), 211 (24), 135 (100), 121 (71), 108 (52), 103 (24), 81 (20), and 77 (67); (6b) (Found: C, 61.5; H, 5.3; S, 32.8. $C_{15}H_{16}S_3$ requires C, 61.6; H, 5.5; S, 32.9%), δ 1.8 (8H, m), 3.9 (2H, m), 7.35 (3H, m), 7.75 (2H, m), and 7.85 (1H, s); ν_{max} 1184 cm^{-1} ; λ_{max} 259 ($\epsilon \times 10^{-3}$ 14.2), 330 (13.5), 430 (20.7), and 615 nm

¹⁹ H. Berlinger and D. Deichmann, *Tetrahedron Letters*, 1967, 1013.

²⁰ E. Klinsberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2934.

²¹ M. G. Voronkov, A. B. Broun, and G. B. Karpenko, *Zhur. obshchei Khim.*, 1949, **19**, 1927 (*Chem. Abs.*, 1950, **44**, 1955g).

(0.167); (7b) (Found: C, 68.4; H, 5.5; S, 26.0. $C_{21}H_{20}S_3$ requires C, 68.4; H, 5.5; S, 26.1%), δ 1.8 (8H, m), 3.9 (2H, m), 7.05 (5H, m), and 7.17 (5H, s); ν_{\max} 1170 cm^{-1} ; λ_{\max} 243 nm ($\epsilon \times 10^{-3}$ 11.7), 259 (11.5), 279 nm (9.25), 319–332 (6.30), 433 (19.8), and 616 nm (0.157).

Photoreaction of (1) at a Higher Concentration of Cyclohexene in Benzene.—The thione (1) (4.22 g, 20 mmol) in benzene (240 ml)–cyclohexene (80 ml) was irradiated for 9 h. Chromatography (petroleum–benzene) gave a red viscous oil (0.23 g), (5b) (4.38 g), and unchanged (1) (0.19 g). The red oil, which was also formed in each reaction of (1) described in the general procedure, gradually decomposed at room temperature in the dark to an orange oil and sulphur, and could not be identified. The addition product (5b), which was an oily material when eluted, became a dark green solid after *ca.* 3 weeks and was recrystallized from ether at solid CO_2 temperature.

Acidic Hydrolysis of (5b).—To a dichloromethane solution (10 ml) of (5b) (293 mg, 1 mmol) was added conc. hydrochloric acid (10 ml) and then ethanol (15 ml). This homogeneous solution was kept at room temperature until it became yellow. Dichloromethane and water were added to the reaction mixture, and the dichloromethane layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the dichloromethane, followed by chromatography, gave sulphur (15 mg), benzoic acid (37 mg, 30%), and *cis*-1,2-cyclohexylene trithiocarbonate (9) (52 mg, 27%) as yellow needles, m.p. 101–103° (from petroleum) (Found: C, 44.2; H, 5.3; S, 50.3. $C_7H_{10}S_3$ requires C, 44.2; H, 5.3; S, 50.5%); ν_{\max} 2950, 2850, 1440, 1090, 1060, 910, and 880 cm^{-1} , δ (CCl_4) 1.2–2.9 (8H, m) and 4.3–4.6 (2H, m), *m/e* 190 (M^+ , 57%), 81 (100), and 80 (54). Cyclohexene was detected by g.l.c. in the reaction mixture from (9) (50 mg, 0.26 mmol) in triethyl phosphite (3 ml). The retention time (polydiethyleneglycol succinate, 2 m, 200°) of the trithiocarbonate obtained in this experiment (41 min) differed from that of the *trans*-isomer synthesized by the reported method¹² (36 min).

Photolysis of (1) in Benzene.—(a) *Under nitrogen.* The thione (1) (2.11 g, 10 mmol) in benzene (200 ml) was irradiated with a high pressure mercury lamp for 14 h. The black solution was chromatographed after the usual work-up. The column warmed, suggesting decomposition of the products on the column. In addition to the starting material (0.344 g), two compounds, (13) (0.384 g) and (14) (0.344 g), were eluted with ether and methanol, respectively. The former was purified by preparative silica gel t.l.c. followed by recrystallization from acetone–dichloromethane to give 5,6-diphenyl-2-thiobenzoylimidazo[1,2-b][1,2,4]-dithiazole as purple crystals which decomposed gradually upon heating, showing no clear melting point (Found: C, 64.7; H, 3.7; N, 9.6; S, 21.8. $C_{25}H_{15}N_3S_3$ requires C, 64.3; H, 3.5; N, 9.8; S, 22.3%); ν_{\max} 3050, 1600, 1490, 1440, 1390, 1330, 1260, 1200, 770, 700, and 680 cm^{-1} , λ_{\max} (CH_2Cl_2) 263 (ϵ 54,100), 319 (22,000), 369 (13,000), and 510 nm (4370), *m/e* 429 (M^+ , 13%), 371 (10), 252 (10), 178 (17), 147 (19), 135 (10), 121 (100), 103 (71), and 77 (33). The imidazoethione (14) was recrystallized from ethanol (m.p. 272–274°) and identified by comparison of its i.r. and u.v. spectra with the reported data²² and the mass spectrum.

(b) *Under oxygen.* The thione (1) (2.11 g, 10 mmol) in benzene (200 ml) was irradiated with a high pressure mercury lamp for 7 h while air was bubbled into the reaction vessel, and the solution, initially orange-red,

became nearly colourless. After removal of a small amount of insoluble material deposited on the wall of the vessel and evaporation of the solvent, the residue was chromatographed to give sulphur (0.21 g), unchanged (1) (0.35 g), compound (14) (0.09 g), and benzamide (0.39 g, 32%).

Photoreaction of Compound (1) with Cyclohexene in Dichloromethane.—The thione (1) (2.11 g, 10 mmol) in dichloromethane (200 ml)–cyclohexene (20 ml) was irradiated with a high pressure mercury lamp for 10 h under cooling with ice–water. Chromatography of the reaction mixture gave sulphur (0.21 g) and compound (5b) (1.46 g, 50%), eluted by carbon tetrachloride and carbon tetrachloride–benzene (1 : 1), respectively.

Photolysis of Compound (5b) with a Low Pressure Mercury Lamp.—Irradiation of (5b) (2.93 g, 10 mmol) in dichloromethane (200 ml) for 20 h, followed by chromatography, gave unchanged (5b) (1.22 g, 42%), compound (1) (0.147 g, 7%), and two other unidentified compounds, one of which was a crystalline material (0.29 g), m.p. 219–221° (decomp.).

Photoreaction of (2) with *cis*- and *trans*-But-2-ene.—External irradiation of the following four solutions in sealed Pyrex tubes was carried out with a high pressure mercury lamp for 14 h at 0°: (a) compound (2) (1.21 g, 5.80 mmol) and *trans*-but-2-ene (7.17 g, 128 mmol) in benzene (80 ml); (b) compound (2) (1.22 g, 5.80 mmol) and *cis*-but-2-ene (7.54 g, 135 mmol) in benzene (80 ml); (c) *trans*-but-2-ene (0.84 g; >99.5% pure) in benzene (10 ml); and (d) *cis*-but-2-ene (1.11 g; >99.5% pure) in benzene (10 ml). From solutions (a) and (b), the olefins were evaporated and trapped in a tube cooled with solid CO_2 –ethanol, and submitted to g.l.c. (benzyl cyanide–silver nitrate, 2 m, 20°). The butene from solution (b) consisted of 98.2% of the *cis*- and 1.8% of the *trans*-isomer, while there was no appreciable change for the solution (a). Neither solution (c) nor (d) showed any detectable change in its g.l.c. Comparison of the methine proton intensities in the n.m.r. spectra ($CDCl_3$) of the green semi-solid residue obtained from solutions (a) and (b) by removal of the benzene and olefins revealed that the *cis*:*trans* ratio [(10) : (11)] of the reaction products from solution (a) and solution (b) were 1 : 5 and 1 : 1, respectively. The reaction mixture from solution (a) was recrystallized from butan-2-ol to give compound (11) containing a small amount of compound (10) (1.50 g, 98%). Two further recrystallizations gave *cis*-4,5-dimethyl-2-thiobenzoylmethylene-1,3-dithiolan (11), m.p. 78–79° (Found: C, 58.7; H, 5.1; S, 36.0. $C_{13}H_{14}S_3$ requires C, 58.6; H, 5.3; S, 36.1%); ν_{\max} 1182 cm^{-1} (C=S), λ_{\max} (EtOH) 258 (ϵ 15,100), 332 (14,000), and 426 nm (18,500) (for n.m.r. data see Table 3). The products from solution (b) were recrystallized twice from butan-2-ol to give a mixture of the *cis*- and *trans*-isomers (10) and (11) (0.72 g, 50%), m.p. 68–70° (Found: C, 58.5; H, 5.1; S, 35.8. Calc. for $C_{13}H_{14}S_3$: C, 58.6; H, 5.3; S, 36.1%); ν_{\max} 1182 and 1160 cm^{-1} (C=S), λ_{\max} (EtOH) 258 (ϵ 15,700), 332 (14,200), and 426 nm (18,600). Attempts to obtain the pure *cis*-isomer were unsuccessful.

Attempted Reactions of Ethylene Trithiocarbonate (15),¹² 4,5-Diphenyl-1,3-dithiole-2-thione (16),²³ and 5-Phenyl-1,2-dithiol-3-one (17)²⁰ with Cyclohexene.—Attempts were made to effect photoreaction of (15)–(17) in benzene (or dichloromethane)–cyclohexene with a high pressure mercury

²² R. Gompper and H. Herlinger, *Chem. Ber.*, 1956, **89**, 2829.

²³ K. M. Pazdro, *Roczniki Chem.*, 1969, **43**, 1089 (*Chem. Abs.*, 1969, **71**, 91,357b).

lamp for 20—26 h. In each case starting material was recovered almost quantitatively. The trithiocarbonate (15) (4.30 g, 32 mmol) in dichloromethane (120 ml)—cyclohexene (52 ml) was irradiated with a low pressure mercury lamp for 48 h. Chromatography of the reaction mixture gave an unidentified compound (0.49 g) and 7,9-dithia-bicyclo[4.3.0]nonane-8-spiro-2'-1',3'-dithiolan (18) [0.54 g, 29% based on (15) consumed] (from methanol), m.p. 117.5—120° (Found: C, 42.8; H, 5.0; S, 51.6. $C_9H_{14}S_4$ requires C, 43.2; H, 5.6; S, 51.2%), δ (CCl_4) 1.2—2.4br

(m, 8H), and 3.1—3.5 (m) and 3.32 (s) (6H in total), δ (C_6D_6) 0.7—2.0br (m, 8H), 2.56—3.08 (m, 4H), and 3.12—3.40br (2H), *m/e* 250 (M^+ , 20%), 222 (48), 190 (24), 168 (75), 140 (25), 136 (18), 114 (12), 81 (100), and 60 (50), along with unchanged (15) (2.21 g) and green tarry material.

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