Reaction of Dehydrodithizone with Benzyne and Diphenylcyclopropenethione. Isolation of *N*-(1,2-Diphenyldiazonia)-1,3-benzothiazole-2-aminate and the Formation of 2-Phenylazo-4,6,7-triphenyl-4*H*-1,3,4-thiadiazepine-5-thione

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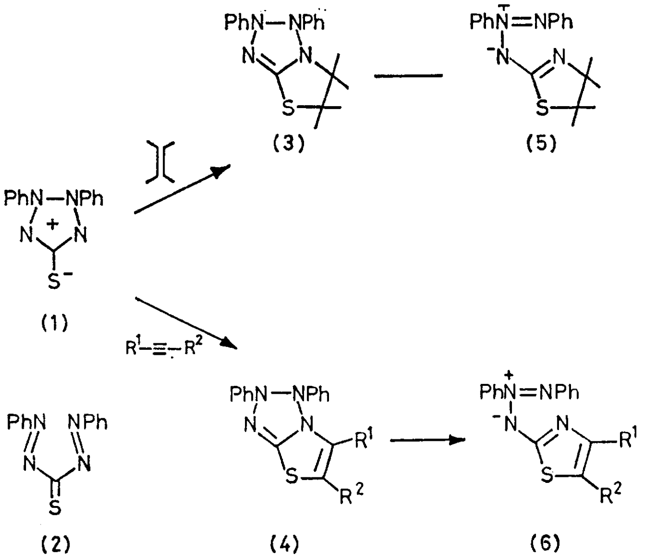
Dehydrodithizone adds benzyne to yield the title compound (7); diphenylcyclopropenethione, on the other hand, gave the thiadiazepine (9). Several other cycloadducts of dehydrodithizone are also described.

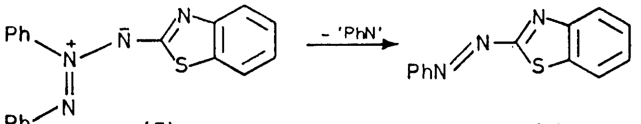
DEHYDRODITHIZONE undergoes addition reactions with many types of olefins and acetylenes.[1] The original assignments [1] of the structures of these adducts were later revised and in many cases confirmed by *X*-ray crystallography.[2,3] The range of reactions was extended [2-4] and their course rationalised by frontier molecular orbital theory.[2] In general, electron-rich multiple-bond compounds give products derived from the acyclic valence-bond isomer (2) of dehydrodithizone, electron-poor olefins and acetylenes yield initially 1,3-dipolar cycloadducts (3) and (4), respectively, of the mesoionic form. Both types of product contain the unknown tetrazoline structure, which is presumably destabilised by the presence of eight π-electrons. They consequently undergo spontaneous ring-opening to yield the 1,5-dipolar azo-imides (5) and (6), some of which could be isolated.[3,4] In the case of the reaction of dehydrodithizone with benzyne (which was conducted at 150 °C), the product, 2-phenylazobenzothiazole (8), was thought to be formed from the intermediate *N*-(1,2-diphenyldiazonia)-1,3-benzothiazole-2-aminate (7) by formal loss of phenylnitrene; the isolation of azobenzene supported this idea.



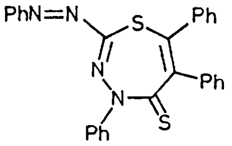
(1) (2) (3) (4) (5) (6)

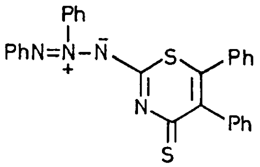
It has now been found that when the addition of benzyne to dehydrodithizone is carried out under milder conditions, *i.e.* in boiling tetrahydrofuran at *ca.* 70 °C, the postulated dipolar compound (7) is obtained as a stable orange-red solid. A single-crystal *X*-ray analysis, details of which will be reported elsewhere, confirmed the structure.

Dehydrodithizone also undergoes ready reaction with diphenylcyclopropenethione in boiling benzene to give glistening purple needles (21%) of a cycloadduct of molecular formula $C_{23}H_{20}N_4S_2$, corresponding to a 1 : 1-adduct. Several structures consistent with such a relationship are possible and, by a combination of ^{13}C n.m.r. data and mass spectral analysis, we have assigned structure (9) to this product.



(7) (8)


(9)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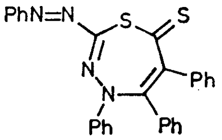
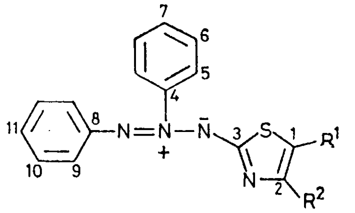

(11)

Table 1 shows ^{13}C chemical shifts for a series of azobenzene-*N*-(thiazol-2-yl)imides prepared from the corresponding electron-deficient dipolarophiles and dehydrodithizone. The close correspondence of the chemical shifts of the various carbon atoms in these three cyclo-

TABLE 1

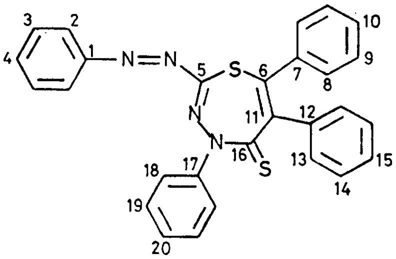
^{13}C Chemical shifts (δ) for several azobenzene-*N*-(thiazol-2-yl)imides



Carbon	$R^1 = R^2 =$ PhCO	$R^1 = R^2 =$ MeO_2C	$R^1,R^2 = -CH=CH-CH=CH-$
1	134.6	137.7	133.9
2	154.7	149.6	150.7
3	163.3	163.7	163.1
4	144.8	144.6	145.7
5	122.9	123.0	122.9
6	129.1	129.3	129.1
7	126.6	126.7	126.5
8	145.5	145.2	146.5
9	125.1	125.5	125.3
10	129.1	129.0	129.0
11	130.9	130.0	130.5

TABLE 2

^{13}C Chemical shifts on the 1,3,4-thiadiazepinethione (9)

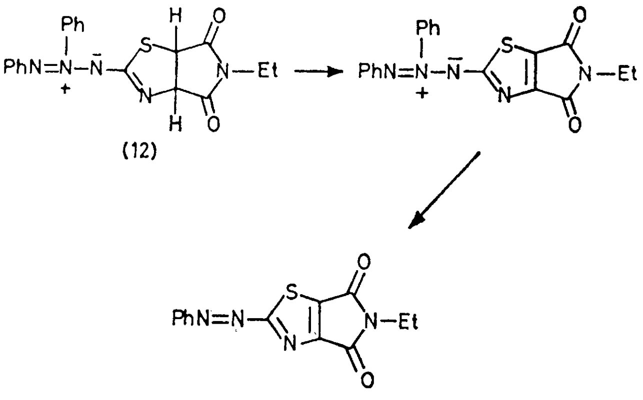


Carbon		Carbon	
1	152.3	11	156.6 *
2	124.0	12	133.7 *
3	127.4	13	128.5 *
4	126.5	14	126.8
5	160.6	15	132.8
6	149.3 *	16	210.2
7	137.2 *	17	141.0
8	129.5 *	18	126.2
9	126.8	19	127.6
10	132.8	20	128.3

* Tentative assignment only.

adducts should be compared with the ^{13}C n.m.r. data for compound (9) shown in Table 2. The corresponding imide structure (10) cannot be readily accommodated by these data, which indicate the presence of a phenylazo-group and an isothiourea carbon atom at δ 160.6, the latter being consistent with reported values in the range δ 140—165. A thiocarbonyl carbon was assigned the furthermost downfield resonance at δ 210.2 which is more consistent with a thioamide C=S (δ *ca.* 190) than with a dithioester C=S (δ *ca.* 225) group.

Strong evidence in support of structure (9) comes from its mass spectrum, which was analysed with the aid of a computer program that calculates the correct peak heights for the isotope pattern of a given empirical formula. The fragment of largest abundance is *m/e* 344, corresponding to the loss of $C_7H_6N_3$ from the molecular ion and probably represented by PhN=NC≡N and a hydrogen atom. As seen in Table 3, the predicted isotope intensities for the ion $C_{21}H_{14}NS_2$ are not in agreement with the observed intensities. After normalization to a 100% scale of the differences between the observed and actual intensities, we find excellent agreement (within 1.8%) with the intensities predicted for a fragment $C_{21}H_{15}NS_2$ (*m/e* 345), corresponding to the loss of phenylazocarbonitrile from the molecular ion. As no ion of *m/e* 178 corresponding to PhN=NPh was present in the spectrum, structure (10) is eliminated from consideration as the azobenzene ion is a characteristic feature of the mass spectra of the azobenzene-*N*-(thiazol-2-yl)imides.



(12)

(13)

Similarly, an abundant ion of *m/e* 121, corresponding to the thiobenzoylium ion $PhC\equiv\overset{+}{S}$, causes us to favour structure (9) over its isomer (11).

Several model compounds were prepared in this study. That from dibenzoylacetylene and dehydrodithizone, described in the Experimental section, is consistent with the product from dimethyl acetylenedicarboxylate. However, with *N*-ethylmaleimide, although the initial mode of addition was consistent with our earlier results,

TABLE 3

Some computer-predicted mass-spectral isotope patterns for (9)

m/e	% Relative intensity	Calc. % at *m/e* 344	Observed difference		Calc. % at *m/e* 345	% Difference
			Actual	Normalized		
344	100.0	100.0				
345	86.77	25.7	61.1	100.0	100.0	0
346	26.84	12.0	14.8	24.2	25.7	−1.5
347	9.37	2.5	6.9	11.3	12.1	−0.8
348	1.88	0.5	1.4	0.7	2.5	−1.8
349	0.33	0.1	0.3	0.5	0.5	0

the intermediate *N*-imide (12) apparently underwent oxidation and subsequent loss of phenylnitrene under the reaction conditions to give (13). The structure of (13) was evident from the mass spectrum (PhN≡N, *m/e* 105) and the n.m.r. spectrum (five aromatic protons).

EXPERIMENTAL

N-(1,2-*Diphenyldiazonia*)-1,3-*benzothiazole*-2-*aminate* (7).—A solution of nitroethane (3 ml) in dry tetrahydrofuran (100 ml) was added during 5 h to a refluxing solution of dehydrodithizone (2.54 g, 0.01 mol) and anthranilic acid (1.4 g) in dry tetrahydrofuran (250 ml) and heating was continued for 1 h. The mixture was cooled, the solvent removed *in vacuo*, and methanol (20 ml) added, whereupon the product separated. It crystallized from methanol as dark-orange *plates* (1.3 g, 39%), m.p. 178—179 °C, *m/e* 330 (M^+, 10%) (Found: C, 69.1; H, 4.25; N, 16.95. $C_{19}H_{14}N_4S$ requires C, 69.12; H, 4.38; N, 16.59%).

4,5-*Dibenzoyl*-N-(1,2-*diphenyldiazonia*)-1,3-*thiazole*-2-*aminate* (6; $R^1 = R^2 =$ COPh).—Dehydrodithizone (2.54 g, 0.01 mol) and dibenzoylacetylene (2.34 g, 0.01 mol) were stirred together at reflux in dry benzene (50 ml) for 3 hours. The crimson solution was evaporated under reduced pressure, and the oily residue crystallized from methanol to afford the product as bright red *prisms* (3.45 g, 77%), m.p. 163—164 °C, $\nu_{max.}$ (KBr) 1 680 cm^{-1} (COPh); δ($CDCl_3$) 8.1—7.4 (m, aromatic); *m/e* 488 (1%, M^+) (Found: C, 71.35; H, 4.2; N, 11.35. $C_{29}H_{20}N_4O_2S$ requires C, 71.29; H, 4.13; N, 11.47).

5-*Ethyl*-2-*phenylazo*-5H-*pyrrolo*[3,4-d]*thiazole*-4,6-*dione* (13).—Dehydrodithizone (2.54 g, 0.01 mol) and *N*-ethylmaleimide (1.25 g, 0.01 mol) were stirred together in dry benzene (50 ml) at reflux for 16 h. The resulting solution was cooled and evaporated under reduced pressure, and the residue was taken up in methanol (10 ml) and allowed to stand overnight. The precipitate was collected by filtration and recrystallized from light petroleum–benzene to afford the product as fluffy yellow *needles* (0.36 g, 13%), m.p. 214—215 °C; δ ($CDCl_3$) 8.2—7.4 (m, 5 H, aromatic), 3.8 (q, 2 H, CH_2, *J* 8.0 Hz), and 1.2 (t, 3 H, Me, *J* 8.0 Hz); *m/e* 286 (6%, M^+) (Found: C, 54.1; H, 3.75; N, 19.3. $C_{13}H_{10}N_4O_2S$ requires C, 54.53; H, 3.52; N, 19.56%).

2-*Phenylazo*-4,6,7-*triphenyl*-4H-1,3,4-*thiadiazepine*-5-*thione* (9).—Dehydrodithizone (1.27 g, 0.005 mol) and diphenylcyclopropenethione (1.10 g, 0.005 mol) were stirred together at reflux in benzene (100 ml) for 1 h. The solution was cooled and concentrated under reduced pressure. Cold methanol (40 ml) was added to induce precipitation of a dark solid, which was collected by filtration and recrystallized from benzene to afford dark purple needles of the *product* (0.50 g, 21%), m.p. 220 °C (decomp.); $\nu_{max.}$ (KBr) 1 490, 1 410, and 1 350 cm^{-1}; δ($CDCl_3$) 8.2—7.8 (m, 2 H, aromatic), 7.7—7.5 (m, 3 H, aromatic), 7.1 (s, 5 H, aromatic), 6.9 (s, 5 H, aromatic), and 6.6 (s, 5 H, aromatic); *m/e* 476 (3%, M^+) (Found: C, 70.25; H, 4.2; N, 12.1. $C_{28}H_{20}N_4S_2$ requires C, 70.38; H, 4.23; N, 11.76%).

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