2-Alkyl-3,5-diaryl-1,3,4-thiadiazolium Perchlorates and Reactions thereof

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2-Alkyl- and 2-aryl-3,5-diaryl-1,3,4-thiadiazolium perchlorates can be prepared from *N'*-arylbenzothiohydrazides by reaction with (a) a carboxylic anhydride–perchloric acid mixture or (b) a nitrile–perchloric acid mixture.

The 2-methyl-3,5-diaryl-1,3,4-thiadiazolium salts can be deprotonated to methine bases which can be trapped by carboxylic anhydrides, thiobenzoylthioglycolic acid, and 1-fluoro-2,4-dinitrobenzene to yield the corresponding derivatives of the methine base; in one instance, the methine base was shown to dimerize in the absence of a trapping agent. Treatment with triethylamine–methanol (or ethanol) gives the 2-alkoxy-2-alkyl-3,5-diaryl-1,3,4-thiadiazole which is also a source of the (trappable) methine base on thermolysis. The 2-aryl series of thiadiazolium salts gives analogous 2-alkoxythiadiazoles under these conditions.

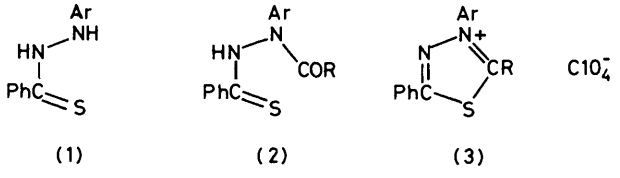
2-Aryl- and 2-alkyl-3,5-diaryl-1,3,4-thiadizaolium ions have been suggested as intermediates in (a) the reaction of 4-mercapto-1,2,3-benzotriazine with a hydrazonoyl halide,[1] and (b) the acylation of *N'*-arylbenzothiohydrazides (1) with an excess of acylating agent.[2] The purpose of the present investigation was to prepare a number of these salts (as perchlorates) and to study their reactions in contexts (a) and (b) above.

A few 1,3,4-thiadiazolium perchlorates have been prepared previously by Boyd and Summers [3] by reaction of *N'*-acyl-*N'*-arylbenzothiohydrazides (2) with acetic anhydride–perchloric acid. We have extended the range of this method by conversion of compounds (2a, b, and c) into the salts (3a, b. and c) in 88, 94, and 86% yield respectively. Insofar as these acylbenzothiohydrazides (2) are isolable products from the acylation of the benzothiohydrazides (1) (*cf.* ref. 2), it seemed reasonable to assume that the benzothiohydrazides themselves could be acylated directly to 1,3,4-thiadiazolium perchlorates (3) in the presence of perchloric acid. This projected route, which parallels a preparation of 1,3,4-oxadiazolium salts from benzohydrazides,[4] was substantiated by independent syntheses of the salts (3a and b) from compound (1a) using acetic and propionic anhydrides, respectively, in yields of 86 and 94%.

We have also developed a synthesis of thiadiazolium salts (3) using a nitrile as the source of C-2 of the heterocyclic ring (Scheme 1). This route was suggested by analogy with a two-stage preparation of methyl thiobenzoate from benzonitrile [5] in which the nitrogen is lost as ammonia (ammonium sulphide). The intermediate salt and its conjugate base would be expected to be unstable under the reaction conditions and to lose ammonia (ammonium perchlorate) to give compounds (3). The lability of one such putative base was demonstrated [6] when, on attempted crystallization of a crude reaction product from methanol or ethanol, the corresponding methyl or ethyl ether was isolated rather than the expected base, presumably *via* the intermediacy of the thiadiazolium ion. In a different context, recent examples of double-bond generation by loss of ammonia have been provided in the indoline series by Landor and his co-workers.[7] Syntheses shown in Scheme 1 were conveniently carried out in acetic acid as solvent, the salts (3) separating on addition of water at the conclusion of the reaction. Results are summarized in the Table; identity of samples prepared by more than one route was established by mixed m.p. determinations and spectral correlations.

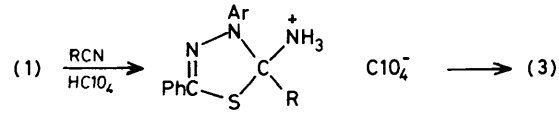
As noted, satisfactory elemental analyses were obtained for all these salts. The ^{1}H n.m.r. spectra of the 2-methyl salts (3a) and (3d) showed signals for the methyl protons at δ (CD_3CN) 3.03 and 2.96, respectively, close to the average value of δ 3.1 (CF_3CO_2H) observed for analogous 1,3,4-oxadiazolium salts.[4] The spectrum of the 2-ethyl salt (3b) was unusual in that the methylene absorption was observed as a multiplet rather than as a quartet. This was not investigated further, but may be due to restricted rotation about the N–aryl bond resulting from *ortho*-substitution of the aryl group. The mass spectra of compounds (3a) and (3d) showed peaks at highest *m/z* values corresponding to loss of perchloric acid from the salts. This is presumably the result of a thermal process leading to the methine base (4a) and (4b), respectively, analogous to that observed with quaternary ammonium salts; a similar phenomenon is observed in the mass spectra of 1-alkyl-2-methylbenzothiazolium iodides.[8]

Proceeding to our study of reactions, we first treated the salt (3e) with ethanol in the presence of triethylamine. This gave the ethyl ether (5e) with properties corresponding to those previously reported for this compound.[6] The salt (3c) similarly gave compound (5c) which after crystallization melted over a range of temperatures and streaked on thin-layer chromatography (t.l.c.); it was, however, identical with a sample prepared by a method analogous to that used pre-



(1) a; Ar = $C_6H_3Br_2$-2,4
b; Ar = Ph

(2),(3) a; Ar = $C_6H_3Br_2$-2,4 , R = Me
b; Ar = $C_6H_3Br_2$-2 4 , R = Et
c; Ar = $C_6H_3Br_2$-2 4 , R = Ph
d; Ar = Ph, R = Me
e; Ar = R = Ph

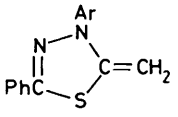


Scheme 1

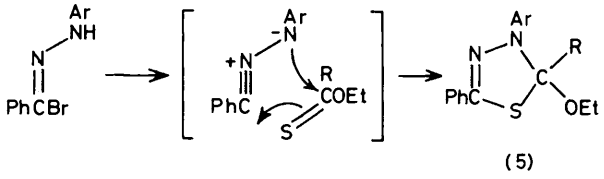
Table. Reactions of benzothiohydrazides (1) with nitriles and perchloric acid to give 1,3,4-thiadiazolium perchlorates (3) (Scheme 1)

Starting materials	Product [a]	Yield (%)	M.p. (°C)	Formula	Found (%) [Requires (%)]
(1a) + MeCN	(3a)	77	173—174	$C_{15}H_{11}Br_2ClN_2O_4S$	C, 35.4; H, 2.2; N, 5.3 [C, 35.3; H, 2.2; N, 5.5]
(1a) + EtCN	(3b)	85	196—198	$C_{16}H_{13}Br_2ClN_2O_4S$	C, 36.6; H, 2.5; N, 5.2 [C, 36.6; H, 2.5; N, 5.3]
(1a) + PhCN	(3c)	76	266—268	$C_{20}H_{13}Br_2ClN_2O_4S$	C, 41.7; H, 2.3; N, 4.9 [C, 41.9; H, 2.3; N, 4.9]
(1b) + MeCN	(3d)	77	149—153	$C_{15}H_{13}ClN_2O_4S$	C, 51.0; H, 3.8; N, 7.7 [C, 51.1; H, 3.7; N, 7.9]
(1b) + PhCN	(3e)	78	215—218 [b]		

[a] Analytical samples were crystallized from acetic acid or acetic acid–diethyl ether. [b] Lit.,[3] m.p. 214—217 °C.



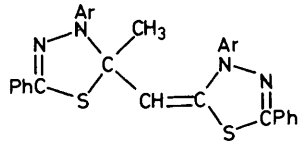
(4) a; Ar = $C_6H_3Br_2$-2,4
b; Ar = Ph



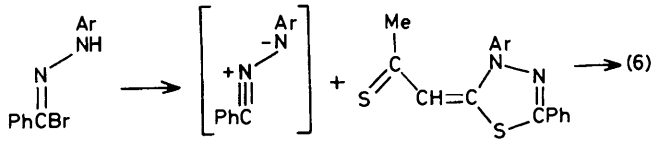
(5)

a; Ar = $C_6H_3Br_2$-2,4, R = Me
b; Ar = $C_6H_3Br_2$-2,4, R = Et
c; Ar = $C_6H_3Br_2$-2,4, R = Ph
d; Ar = Ph, R = Me
e; Ar = R = Ph

Scheme 2



(6) Ar = $C_6H_3Br_2$-2,4



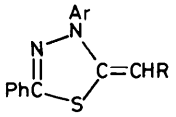
Scheme 3

viously for compound (5e) (Scheme 2).[6] The streaking on t.l.c. is thought to be due to partial hydrolysis of compound (5c), presumably *via* the thiadiazolium ion (3c), to give the mixed hydrazide (2c). The hydrolysis of compound (5c) to (2c) was separately demonstrated by heating the thiadiazole in boiling, aqueous acetonitrile.

The ^{1}H n.m.r. spectrum of compound (5c) was interesting in that the methylene absorption consisted of a multiplet rather than a quartet, *i.e.* the methylene protons are non-equivalent. Similar cases have been noted previously, *viz.* the case of compound (5d)[9] and that of the compound corresponding to (5c) in which the 2-substituent is *o*-aminophenyl instead of phenyl.[1] In these compounds, the methylene protons are diastereotopic (chiral centre at C-2) and observation of these protons (H_A and H_B) as part of an ABX_3 spin system is to be expected.[10,11]

The conditions for the conversions (3c) ⟶ (5c), (3e) ⟶ (5e) are probably general since the salt (3a) gave the corresponding methyl ether when methanol was used as the solvent for reaction. The structure of this latter ether followed from microanalysis and from its ^{1}H n.m.r. spectrum, but the compound deteriorated on keeping or on attempted recrystallization, and it melted with decomposition. The mass spectrum showed the peak at highest *m/z* value corresponding to loss of methanol from the ether, with subsequent fragmentation of this ion; no molecular ion was detectable. This suggested a ready thermal loss of methanol from the ether to give the methine base (4a). In fact, such a thermal reaction conducted in n.m.r. tubes at temperatures of *ca.* 70 °C showed progressive loss of the methyl ether with accompanying formation of methanol and, as an artefact, a dimer of compound (4a). This dimer could be readily prepared by treatment of compound (3a) with triethylamine in dry acetonitrile. The structure of the dimer was assigned as (6) on the basis of its ^{1}H n.m.r. spectrum, which showed singlets at δ ($CDCl_3$) 4.3 and 1.8 with a peak ratio 1 : 3 for the non-aromatic protons. This situation is reminiscent of that in the benzothiazolium salt series where an intermediate methine base was observed to dimerize under the reaction conditions used;[12] the dimer (6) presumably forms in a similar way by addition of the nucleophilic compound (4a) to the salt (3a) during base-treatment of the latter. Interestingly, a more deep-seated change is observed in an example from the closely related series of 1,3,4-oxadiazolium salts (12 h reaction time); the first-formed dimer of the methine base analogous to compound (6) is thought to undergo a series of cleavage and cyclization reactions to give the isomeric dimer which is finally obtained.[13]

The structure (6) assigned to the dimer of compound (4a) is supported by an alternative synthesis from the 3-aryl-2,3-dihydro-5-phenyl-2-thioacetylmethylene-1,3,4-thiadiazole[14] as shown in Scheme 3. The resulting sample of the dimer (6) contained a small amount of entrained thiadiazole starting material, but it was possible to confirm the identify of the product by ^{1}H n.m.r. and t.l.c. comparisons. Compound (6) reverts to the salt (3a) on treatment with perchloric acid, presumably by reversal of the reaction involved in formation of the dimer (6) from the salt (3a), *i.e.*



(7)

a; Ar = $C_6H_3Br_2$-2,4, R = COMe
b; Ar = $C_6H_3Br_2$-2,4, R = $C_6H_3(NO_2)_2$-2,4
c; Ar = $C_6H_3Br_2$-2,4, R = COEt
d; Ar = Ph, R = COMe
e; Ar = $C_6H_3Br_2$-2,4, R = CSPh

protonation of (6), cleavage to (3a) and (4a), and further protonation of (4a) to give (3a).

The thermal decomposition of the ethers (5) could, in principle, be put to use by incorporating a trapping agent for the methine base (4) produced as the primary product. For example, thermolysis of such an ether in acetic anhydride should permit acetylation of the intermediate methine base; in this way, the known [2] 2-acetylmethylene-3-(2,4-dibromophenyl)-2,3-dihydro-5-phenyl-1,3,4-thiadiazole (7a) was prepared. This reaction simulated a late stage in the acetylation of *N'*-arylbenzothiohydrazides and is consistent with that mechanism.[2] In another experiment, compound (5a), generated *in situ* from the salt (3a) and ethanol–triethylamine, was thermolysed in the presence of 1-fluoro-2,4-dinitrobenzene to give compound (7b).

2-Methylthiadiazolium salts such as (3a) and (3d) can be deprotonated by base and hence can similarly be used as synthetic intermediates, provided that conditions for dimerization of the resulting methine base are precluded. Acylation in particular was shown to be feasible by conversion of compound (3a) into compound (7a) by reaction with acetic anhydride–sodium acetate, and into compound (7c) by reaction with propionic anhydride–sodium hydroxide. Acetyl chloride–pyridine similarly transformed the salt (3d) into compound (7d). The scope of such reactions can evidently be extended since compound (3a) gave the thiobenzoyl derivative (7e) on treatment with thiobenzoylthioglycolic acid in ethanol–triethylamine.

In summary, the results obtained in this work are consistent with previously suggested reaction mechanisms [1,2] and demonstrate further the versatility of such salts as (3a) and (3d) as well as the related 2-ethers [*e.g.* (5)] as intermediates for synthetic elaboration.

Experimental

Instrumental techniques were as noted in previous publications [2,14] except for the choice of solvent, noted herein, for ^1H n.m.r. determinations.

1,3,4-*Thiadiazolium Perchlorates* (3).—The following reactions are representative.

(i) The general procedure of Boyd and Summers [3] was followed. The benzothiohydrazide (1) or acylbenzothiohydrazide (2) (1.0 g) was suspended in acetic anhydride (8 ml) and perchloric acid (0.8 ml) was added dropwise. If the product did not crystallize out of the reaction mixture, diethyl ether was added and the resulting gum was triturated with fresh diethyl ether until the product had crystallized.

Thus, compound (2b) afforded 3-(2,4-*dibromophenyl*)-2-*ethyl*-5-*phenyl*-1,3,4-*thiadiazolium perchlorate* (3b) (1.1 g, 94%) as needles, m.p. 196—198 °C (from acetic acid–diethyl ether); $\nu_{max.}$ 1 630, 1 510, 1 480, 1 460, 1 440, 1 090, 880, and 850 cm^{-1}; δ (CD_3CN) 1.57 (3 H, t, Me), 3.2 (2 H, m, CH_2), and 7.5—8.1 (8 H, m, ArH).

The benzothiohydrazide (1a) with propionic anhydride similarly afforded compound (3b) (1.27 g, 94%), m.p. and mixed m.p. 196—198 °C (from acetic acid–diethyl ether).

(ii) The benzothiohydrazide (1) (1.0 g) and the nitrile RCN (1.2 equiv.) in acetic acid (2 ml) containing perchloric acid (1 ml) were heated at reflux for 5 min. The suspension was allowed to cool and water (20 ml) was then slowly added to the stirred mixture to dissolve the white insoluble solid (ammonium perchlorate). The required thiadiazolium salt either precipitated spontaneously at this stage or formed an oil.

Thus, *N'*-phenylbenzothiohydrazide (1b) and acetonitrile afforded 2-*methyl*-3,5-*diphenyl*-1,3,4-*thiadiazolium perchlorate* (3d) (1.2 g, 77%), m.p. 149—153 °C (precipitated from acetic acid on the addition of diethyl ether); $\nu_{max.}$ 1 600, 1 525, 1 500, 1 460, 1 340, 1 100, 790, and 700 cm^{-1}; δ (CD_3CN) 2.96 (3 H, s, Me) and 7.5—8.1 (10 H, m, 2 × Ph); *m/z* 252 (salt − $HClO_4$).

2-*Ethoxy*-2,3-*dihydro*-2,3,5-*triphenyl*-1,3,4-*thiadiazole* (5e).—A solution of 2,3,5-triphenyl-1,3,4-thiadiazolium perchlorate (3e) (1.0 g) in dry ethanol (10 ml) containing triethylamine (0.67 ml) was heated at reflux for 15 min. The precipitate, obtained after keeping the solution overnight, was collected by filtration and was crystallized from ethanol to give compound (5e) (540 mg, 63%) as prisms, m.p. 126—128 °C (lit.,[6] 128.5—129.5 °C).

3-(2,4-*Dibromophenyl*)-2-*ethoxy*-2,3-*dihydro*-2,5-*diphenyl*-1,3,4-*thiadiazole* (5c).—(i) A suspension of compound (3c) (1.0 g) in dry ethanol (25 ml) containing triethylamine (0.6 ml) was heated at reflux for 30 min. The crystals which separated upon cooling were collected by filtration and were washed with ethanol. Recrystallization from ethanol afforded 3-(2,4-*dibromophenyl*)-2-*ethoxy*-2,3-*dihydro*-2,5-*diphenyl*-1,3,4-*thiadiazole* (5c) (810 mg, 79%) as prisms, m.p. 155—163 °C (Found: C, 50.7; H, 3.5; N, 5.2. $C_{22}H_{18}Br_2N_2OS$ requires C, 51.0; H, 3.5; N, 5.4%); $\nu_{max.}$ 1 475, 1 445, 1 330, 1 225, 1 065, 750, and 685 cm^{-1}; δ ($CDCl_3$) 1.37 (3 H, t, CH_2Me), 3.66 (2 H, m, CH_2Me), and 7.11—7.85 (13 H, m, ArH); *m/z* 516 (1%, M^+), 471 (3, $[M - C_2H_5O]^+$), 437 (5, $[M - Br]^+$), 391 (1), 367 (3, $[M - C_2H_4 - C_6H_5CS]^+$), 350 (10, 367 − OH), 336 (1, 350 − N), and 105 (100, C_6H_5CO).

(ii) Triethylamine (0.63 ml) was added to a solution of *N*-α-bromobenzylidene-*N'*-2,4-dibromophenylhydrazine [15] (1.0 g) and *O*-ethyl thiobenzoate (770 mg) in dry benzene (25 ml). After the suspension had been stirred for 30 min, the precipitate was collected by filtration, washed with water, and was crystallized from ethanol to afford compound (5c) (1.03, 87%) as prisms, m.p. 155—165 °C; the ^1H n.m.r. spectrum was identical with that of the foregoing sample.

Hydrolysis of Compound (5c).—A solution of compound (5c) (200 mg) in acetonitrile (20 ml) containing water (5 ml) was boiled under reflux overnight. The solution was allowed to cool and further water was then added. The precipitate was collected by filtration, dried, and crystallized from methylene dichloride–hexane to afford *N*-(2,4-dibromophenyl)-*N'*-thiobenzoylbenzohydrazide (2c) (140 mg, 74%), m.p. and mixed m.p. 127—129 °C.

3-(2,4-*Dibromophenyl*)-2,3-*dihydro*-2-*methoxy*-2-*methyl*-5-*phenyl*-1,3,4-*thiadiazole*.—To a solution of 3-(2,4-dibromophenyl)-2-methyl-5-phenyl-1,3,4-thiadiazolium perchlorate (3a) (1.0 g) in a mixture of dry acetonitrile (25 ml) and dry methanol (25 ml) was added triethylamine (0.55 ml). The solu-

tion was kept in a refrigerator for 24 h and the crystals which formed were collected by filtration, washed with dry methanol and dried *in vacuo* to give 3-(2,4-*dibromophenyl*)-2,3-*dihydro*-2-*methoxy*-2-*methyl*-5-*phenyl*-1,3,4-*thiadiazole* as pale orange prisms (640 mg, 80%), m.p. 115—120 °C (decomp.) (Found: C, 43.7; H, 3.3; N, 6.3. $C_{16}H_{14}Br_2N_2OS$ requires C, 43.5; H, 3.2; N, 6.3%); $\nu_{max.}$ 1 475, 1 375, 1 345, 1 110, 850, 825, 760, and 685 cm^{-1}; δ ($CDCl_3$) 1.91 (3 H, s, 2-Me), 2.31 (3 H, s, OMe), and 7.2—7.8 (8 H, m, ArH); *m/z* 408 (21%, $[M - MeOH]^+$), 329 (44, 408 − Br), 250 (100, 329 − Br), 233 (5, $C_6H_3Br_2$), 226 (11, 329 − C_6H_5CN), 180 (9, 226 − CH_2S), and 175 (9, $C_9H_7N_2S$).

Reaction of Compound (3a) *with Base*.—To a solution of compound (3a) (1.0 g) in dry acetonitrile (15 ml) was added triethylamine (0.55 ml). After the mixture had been stirred for 30 min the oil which initially deposited had solidified. The solid was collected by filtration and was washed with water and dried to afford *compound* (6) (650 mg, 81%) as a yellow solid, m.p. 157—160 °C (Found: C, 44.0; H, 2.6; N, 6.8. $C_{30}H_{20}Br_4N_4S_2$ requires C, 44.0; H, 2.5; N, 6.8%); $\nu_{max.}$ 1 600, 1 470, 1 380, 1 270, 1 210, 980, 765, and 690 cm^{-1}; δ ($CDCl_3$) 1.8 (3 H, s, Me), 4.3 (1 H, s, =CH), and 7.2—8.0 (16 H, m, ArH); when a low probe temperature was used, the mass spectrum showed *m/z* 408 as the highest peak value, corresponding to the monomeric species (4a).

Alternative Synthesis of Compound (6).—To a suspension of 3-(2,4-dibromophenyl)-2,3-dihydro-5-phenyl-2-thioacetylmethylene-1,3,4-thiadiazole (500 mg) and *N*-α-bromobenzylidene-*N'*-2,4-dibromophenylhydrazine [15] (460 mg) in dry acetonitrile (20 ml) was added triethylamine (0.5 ml). The suspension was stirred for 2 h, after which the insoluble yellow solid was collected by filtration, washed with water, and dried to afford compound (6) as a yellow solid (720 mg, 82%), m.p. 149—154 °C, mixed m.p. 149—156 °C. The ^1H n.m.r, spectrum was identical with that already described except for a small peak at δ 2.7 which was attributed to the presence of some of the unchanged thioacetylmethylene compound. This was confirmed by t.l.c.

Reaction of Compound (6) *with Acid*.—A solution of compound (6) (500 mg) in acetic acid (5 ml) containing perchloric acid (1 ml) was boiled under reflux for 30 min. The solution was allowed to cool and then diethyl ether was added to the point of incipient turbidity. This precipitated the salt (3a) (380 mg, 61%), m.p. and mixed m.p. 171—173 °C. The ^1H n.m.r. spectrum was identical with that already described.

2-*Acetylmethylene*-3-(2,4-*dibromophenyl*)-2,3-*dihydro*-5-*phenyl*-1,3,4-*thiadiazole* * (7a).—A solution of 3-(2,4-dibromophenyl)-2,3-dihydro-2-methyl-2-methoxy-5-phenyl-1,3,4-thiadiazole (500 mg) in acetic anhydride (5 ml) was boiled under reflux for 30 min. The red solution was then poured into water and the precipitate which formed when the mixture was stirred was collected by filtration. Chromatography (silica gel; benzene as eluant) and crystallization from acetonitrile afforded compound (7a) (301 mg, 59%) as tan-coloured prisms, m.p. 155—157 °C (lit.,[2] 155—156 °C).

Alternative Synthesis of Compound (7a).—A solution of the perchlorate (3a) (1.8 g) in acetic anhydride (10 ml) containing sodium acetate (320 mg) was boiled under reflux for 30 min. The usual work-up afforded the title thiadiazole (1.21, 76%) as tan-coloured prisms which, after recrystallization, had m.p. and mixed m.p. 155—157 °C.

3-(2,4-*Dibromophenyl*)-2-(2,4-*dinitrobenzylidene*)-2,3-*dihydro*-5-*phenyl*-1,3,4-*thiadiazole* (7b).—A solution of compound (3a) (1.0 g) and 1-fluoro-2,4-dinitrobenzene (1.0 g) in dry ethanol (20 ml) containing triethylamine (0.54 ml) was boiled under reflux for 1 h. The mixture was cooled and the precipitate was collected by filtration and crystallized from methanol–pyridine to afford 3-(2,4-*dibromophenyl*)-2-(2,4-*dinitrobenzylidene*)-2,3-*dihydro*-5-*phenyl*-1,3,4-*thiadiazole* (7b) (910 mg, 81%) as dark-red prisms, m.p. 262—264 °C (Found: C, 44.0; H, 2.3; N, 9.7. $C_{21}H_{12}Br_2N_4O_4S$ requires C, 43.8; H, 2.1; N, 9.7%).

4-Fluoronitrobenzene did not react under these conditions.

3-(3,4-*Dibromophenyl*)-2,3-*dihydro*-5-*phenyl*-2-*propionylmethylene*-1,3,4-*thiadiazole* † (7c).—A solution of the perchlorate (3a) (1.0 g) in propionic anhydride (5 ml) containing a pellet of sodium hydroxide was boiled under reflux for 30 min. The usual work-up afforded the thiadiazole (7c) (500 mg, 55%) as tan-coloured needles (95% ethanol), m.p. 116—118 °C (lit.,[2] 117—118 °C).

2-*Acetylmethylene*-2,3-*dihydro*-3,5-*diphenyl*-1,3,4-*thiadiazole* ‡ (7d).—The perchlorate (3d) (1.0 g) was added to an ice-cooled suspension of dry pyridine (10 ml) containing acetyl chloride (0.26 ml). The suspension was stirred at room temperature until a solution was obtained (*ca.* 1 h). The solution was then poured into water (100 ml) and the precipitate which formed when the mixture was stirred was collected by filtration. Repeated crystallization from ethanol afforded the thiadiazole (7d) (420 mg, 50%) as grey needles, m.p. 151—153 °C (lit.,[2,16] 152—153 °C).

3-(2,4-*Dibromophenyl*)-2,3-*dihydro*-5-*phenyl*-2-*thiobenzoylmethylene*-1,3,4-*thiadiazole* § (7e).—Triethylamine (0.8 ml) was added to a stirred suspension of the perchlorate (3a) (1.5 g) in dry ethanol (50 ml). After 5 min, thiobenzoylthioglycolic acid (3.1 g) was added and the suspension was boiled under reflux for 20 h. The solvent was removed and the red, solid residue was dissolved in chloroform (100 ml). The chloroform solution was washed in turn with 5% sodium hydroxide (2 × 100 ml) and water (3 × 100 ml) and was then dried (sodium sulphate). Evaporation of the chloroform, chromatography of the residue (silica gel; benzene as eluant), and crystallization from chloroform–light petroleum (b.p. 30—60 °C) gave the thiadiazole (7e) (1.0 g, 68%) as orange needles, m.p. 224—227 °C (lit.,[14] 224—227 °C).

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* Systematic name: 2-*Acetonylidene*-3-(2,4-*dibromophenyl*)-2,3-*dihydro*-5-*phenyl*-1,3,4-*thiadiazole*.
† Systematic name: 3-(2,4-*Dibromophenyl*)-2,3-*dihydro*-2-(2-*oxobutylidene*)-5-*phenyl*-1,3,4-*thiadiazole*.
‡ Systematic name: 2-*Acetonylidene*-2,3-*dihydro*-3,5-*diphenyl*-1,3,4-*thiadiazole*.
§ Systematic name: 3-(2,4-*Dibromophenyl*)-2,3-*dihydro*-5-*phenyl*-2-*thiophenacylidene*-1,3,4-*thiadiazole*.

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