On the Alkylation of Multisite Aromatic Heterocycles. Part 2.[1] Formation and Thermal Decomposition of 4-Alkyl-5-alkylimino-1,2,3,4-thiatriazolines

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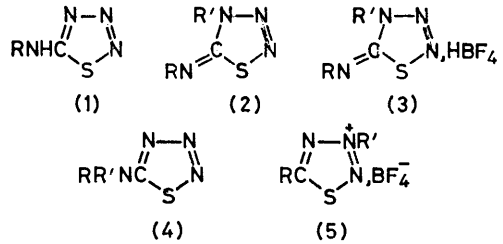
Hitherto unknown 4-alkyl derivatives of 5-alkylimino-1,2,3,4-thiatriazolines have been obtained in good yields by alkylation of 5-alkylaminothiatriazoles with trialkyloxonium tetrafluoroborates. 5-Arylamino- and 5-sulphonylamino-thiatriazoles are similarly alkylated in the 4-position. The dialkyliminothiatriazolines undergo thermal decomposition with loss of nitrogen and sulphur to form carbodi-imides. Decomposition can be induced by adding electron-rich alkenes or heterocumulenes in contrast to the corresponding 4-alkyl-5-arylimino- and 4-alkyl-5-sulphonylimino-thiatriazolines.[2]

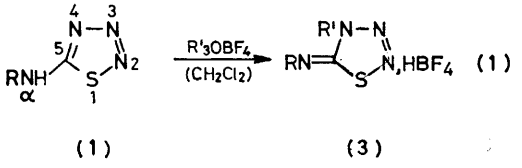
5-ARYLAMINO- and 5-sulphonylamino-1,2,3,4-thiatriazoles (1) are reported to be alkylated in position 4 (2; R′ = Me) and/or at the α position (4) by diazomethane depending on the aryl group.[3] In contrast to this the corresponding 5-aryl- and 5-alkylthio-1,2,3,4-thiatriazoles were found to be alkylated at position 3 (5; R′ = Et) by



SCHEME 1

triethyloxonium tetrafluoroborate.[1] The latter structure assignment, based on ^1H, ^{13}C, and ^{15}N n.m.r. data, was later confirmed by an *X*-ray structure determination.[4] We have now extended our work by studying the alkylation of 5-amino-1,2,3,4-thiatriazoles (1) with trialkyloxonium tetrafluoroborates.

Alkylation of Aminothiatriazoles with Trialkyloxonium Tetrafluoroborates.—In contrast to the alkylation of α-monosubstituted aminothiatriazoles with diazomethane,[3] which may give rise to a mixture of isomers, only single products in good yields are obtained by alkylation with trialkyloxonium tetrafluoroborates. On the basis of the discussion below it is concluded that alkylation takes place in position 4 [equation (1)].



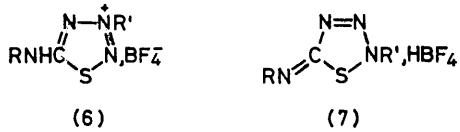
Physical data and yields for the salts (3a—f) and the corresponding free bases (2a—g) are compiled in Tables 1 and 2. Isomeric 5-dialkylaminothiatriazoles have been included in Table 2 for the sake of comparison. The alkylated compounds were hitherto unknown except (2e) and (2g). These had previously been prepared by the diazomethane method and formulated as the 4-methylated products.[3] We find identical physical data (m.p., ^1H n.m.r., and i.r. spectra) for the compounds obtained by alkylation of (1; R = Ph or $MeC_6H_4SO_2$) with either diazomethane or trimethyloxonium tetrafluoroborate. Although this points to the conclusion that all alkylated products here obtained are 4-alkylated, a more detailed structure discussion appears necessary.

TABLE 1

Reaction products of (1) with trialkyloxonium tetrafluoroborates: 4,5-disubstituted iminothiatriazolines (2) and (3)

	R	R′	Yield of (3)	M.p. (°C) of (3) *	M.p. (°C) of free base (2)
a	Me	Me	56	115	Oil
b	Et	Me	73	133	Oil
c	Me	Et	29	87—88	Oil
d	Et	Et	38	142	Oil
e	Ph	Me	100	162	68—69
f	Ph	Et	91	164	31—32
g‡	*p*-$MeC_6H_4SO_2$	Me	57		117—118

* All decomposed at m.p. ‡ Isolated as the free base (2).



Ring alkylation is immediately evident from the ^1H n.m.r. data in Table 2 as shown by the nonequivalence of the two methyl (2a) or two ethyl (2d) groups. Furthermore, the methyl and ethyl substituents display

[1] Part 1, A. Holm, K. Schaumburg, N. Dahlberg, C. Christophersen, and J. P. Snyder, *J. Org. Chem.*, 1975, **40**, 431.

[2] (*a*) G. L'abbé, E. Van Loock, R. Albert, S. Toppet, G. Verhelst, and G. Smets, *J. Amer. Chem. Soc.*, 1974, **96**, 3973; (*b*) G. L'abbé, G. Verhelst, C. C. Yu, and S. Toppet, *J. Org. Chem.*, 1975, **40**, 1728; (*c*) G. L'abbé and C. C. Yu, *J. Heterocyclic Chem.*, 1976, **13**, 883; (*d*) G. L'abbé, G. Verhelst, and S. Toppet, *J. Org. Chem.*, 1976, **41**, 3403.

[3] (*a*) R. Neidlein and J. Tauber, *Arch. Pharm.*, 1971, **304**, 687; (*b*) R. Neidlein and K. Salzmann, *Synthesis*, 1975, 52.

[4] T. Ottersen, *Acta Chem. Scand.*, 1976, **A30**, 351.

δ values expected of *N*-alkyl salts [5] rather than *S*-alkyl salts.[6] Thus the structures to be further considered are (3), (6), and (7).

Compounds (2a—d) are thermally labile, decomposing with formation of nitrogen, sulphur, and carbodi-imides [equation (5)]. There is no indication of alkyl migration (n.m.r.) during this process. Compound (2e) has previously been shown to fragment around 120 °C with loss

TABLE 2

^{1}H N.m.r. values of iminothiatriazolines (2) and aminothiatriazoles (4) (δ, CCl_4, $SiMe_4$ as internal standard). Chemical shifts for tetrafluoroborate salts (3) are given in parentheses (D_2O, DSS as internal standard)

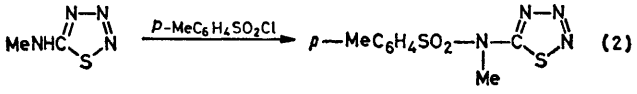
	RN=C·S·N=N-NR′				R_2N–C=N·N=N·S
	(2a)	(2b)	(2c)	(2d)	
δ′CH_3	3.75 (4.17)	3.77 (4.21)			
δ′CH_3CH_2			4.21 (4.60)	4.20 (4.65)	
δ′CH_3CH_2			1.46 (1.58)	1.46 (1.64)	
δCH_3	2.99 (3.26)		2.98 (3.27)		3.27
δCH_3CH_2		3.00 (3.55)		3.01 (3.64)	3.61
δCH_3CH_2		1.23 (1.39)		1.23 (1.43)	1.30

of nitrogen and formation of 2-methylaminobenzthiazole.[3a] Neither of these two types of reaction product is compatible with structure (6). This result is further stressed by the pronounced thermal stability of true 3-alkylated thiatriazolium salts (5), which may be heated to *ca.* 200 °C without decomposition.[1] Although structure (2) [(3)] appears to be the most obvious candidate, apparently leading directly to the observed carbodi-imide on degradation, structure (7) cannot be excluded without comment since a bond might be formed between C(5) and N(2) during decomposition. However, investigation of the mass spectra of (2a—g) reveals that they exhibit loss of N_2S, which by the metastable-defocusing technique is found to take place in one step from the molecular ion. This shows that the ring alkyl group is located in position 4, provided, of course, that migration of alkyl groups in the molecular ion is excluded.

Furthermore, we find that toluene-*p*-sulphonyl chloride reacts with (1; R = Me) like dimethyl sulphate [3a] to give the α,α-disubstituted thiatriazole (4g) [equation (2)], which is identical (m.p. and i.r.) with the compound obtained together with (2g) by Neidlein and his coworkers by the diazomethane method [3b] [equation (3)].

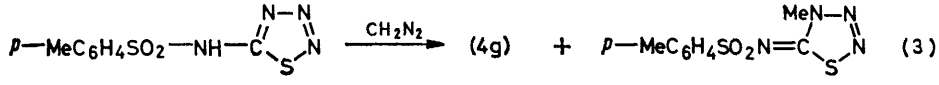
Finally toluene-*p*-sulphonyl isothiocyanate was treated with methyl azide, and the product obtained was found to be identical with the above-mentioned (2g) [equation (4)]. This is the method used by L'abbé *et al.* [2a] for preparation of thiatriazolines. The thiatriazolines obtained were assigned structure (2; R′ = Bu or $PhCH_2$, R = *p*-$XC_6H_4SO_2^-$).

Thermal Properties of 4-Alkyl-5-alkylimino-1,2,3,4-thiatriazolines.—All 4-alkyl-5-alkyliminothiatriazoline tetrafluoroborates (3a—d) are crystalline solids which decompose when heated to their m.p. (Table 1). They may be stored for an indefinite time at room temperature and serve as convenient sources of the free bases. These



(1) (4g)

may be liberated by treatment with sodium hydrogen carbonate and are obtained as thermally labile oils decomposing slowly around 40—60 °C and rapidly at 125 °C with formation of sulphur, nitrogen, and carbodi-imides [equation (5)].



(2g)

The thermal lability of the free bases is, however, considerably influenced by the purity of the starting material, and thiatriazolines purified by high-vacuum sublimation show strongly enhanced stability. A closer study has revealed that the carbodi-imides formed on thermal decomposition react with undecomposed thiatriazoline (see below). This, in part, explains the low yields of isolable carbodi-imide. The question of possible intermediates in the decomposition of thiatriazolines is discussed below.

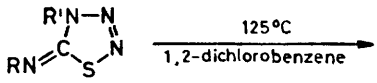
(2g)

Reaction of 4-Alkyl-5-alkyliminothiatriazolines with Dipolarophiles.—L'abbé *et al.* have previously shown that 5-sulphonylimino-4-alkyl-1,2,3,4-thiatriazolines are

[5] M. Begtrup, personal communication.

[6] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, 1966, **88**, 5747.

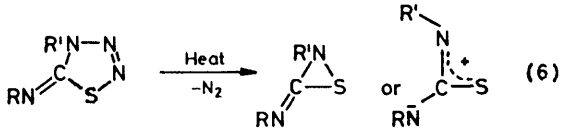
thermolysed at 45—80 °C to sulphonylcarbodi-imides, analogously to the reaction in equation (5).[2] In the presence of various dipolarophiles such as enamines, ynamines, phosphorus ylides, carbodi-imides, isocyanates, isothiocyanates, and nitriles cycloaddition products are obtained which are formally derived from thiaziridines [equation (6)].[2] Kinetic experiments showed that the rate of decomposition of 4-benzyl-5-tosylimino-1,2,3,4-thiatriazoline is not influenced by the presence of enamines. This result demonstrates that a discrete



$$R'N{=}C{=}NR + N_2 + S \qquad (5)$$

Yields of carbodi-imide:
(2b), 7%, (2c), 16%, (2d), 52%

intermediate is formed by a unimolecular process, but it does not distinguish between a thiaziridine and its open-chain counterpart [equation (6)].[2]



(6)

(2)

R' = $PhCH_2$, R = p-$MeC_6H_4SO_2$

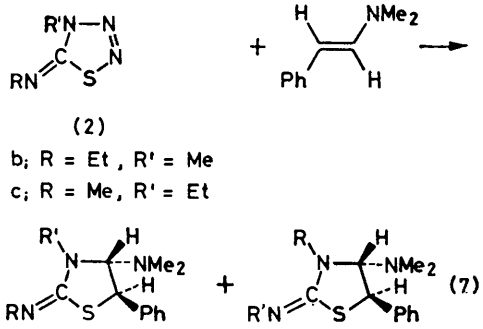
Although we find that compounds (2a—d) react rapidly with dipolarophiles at 40 °C, the mechanism differs from that above. Nitrogen is evolved immediately on addition of electron-rich alkenes or heterocumulenes such as enamines, carbodi-imides, isocyanates, isothiocyanates, or styrene to solutions of (2a—d) which are relatively stable at room temperature. A closer examination of the reaction between diphenylketen and solutions of (2a—c), described below, indicate that these reactions may be complex. It is not possible on this basis to decide whether the decomposition of 4,5-dialkyliminothiatriazolines to carbodi-imides involves an intermediate. Electron-poor alkenes such as *trans*-stilbene, diethyl fumarate and maleate, and fumaronitrile do not cause nitrogen evolution from solutions of (2a—d). Even on heating cycloaddition products were not isolated with the latter compounds, although decomposition was induced. Addition of bases such as benzylamine had no influence on the decomposition rate.

(*a*) *Reaction with* β-NN-*dimethylaminostyrene.* Nitrogen is immediately evolved on dissolving thiatriazoline (2b) or (2c) in neat β-*NN*-dimethylaminostyrene at room temperature. The elemental analysis and mass spectrum of the common adduct ($M^{+\cdot}$ 263 *m/e*) isolated by preparative t.l.c., are in agreement with structures (11) and (12) (Calc. 263 *m/e*) [equation (7)].

270 MHz ^{1}H N.m.r. spectroscopy reveals the existence of 2 AB patterns in the adduct with δ_A 4.35, δ_B 4.31, J = 2.05 Hz and δ'_A 4.37, δ'_B 4.23, J = 2.25 Hz respectively, corresponding to an almost equal mixture of compounds formulated as (11) and (12). It is not possible directly from the coupling constants to deduce whether the vicinal methine protons are *cis* or *trans*.

Generally values from 1—10 Hz may be found for both *cis*- and *trans*-protons in heterocyclic five-membered rings.[7] On the other hand, there is no indication of further isomers from the ^{1}H n.m.r. spectrum, which shows that only a *cis*- or a *trans*-mixture is formed. The starting enamine is of the thermodynamically stable *trans*-configuration [8] and the thermodynamically stable forms of the adduct are clearly also the *trans*-forms. Whether the reaction leading to (11) and (12) is concerted or stepwise, the expected configuration is therefore *trans*.

The i.r. spectrum of the adduct is characterized by a



(2)

b; R = Et, R' = Me
c; R = Me, R' = Et

(7)

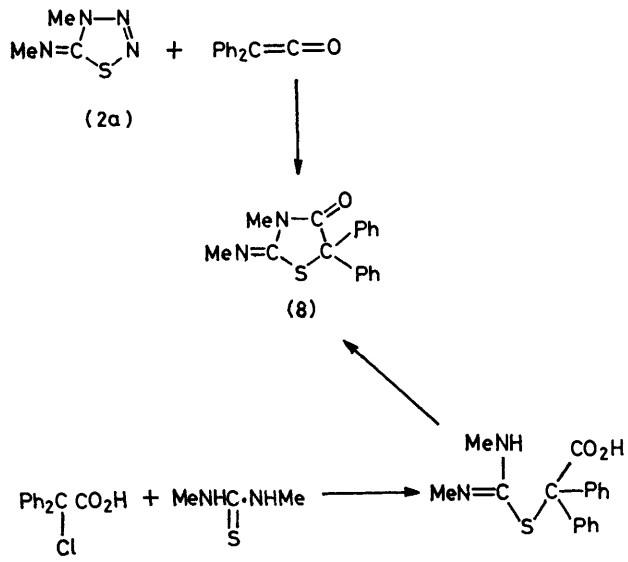
(11) (12)

broad, strong band at 1 640 cm^{-1} similar to that of precursors (2a—e), assigned to the C=N group (1 620—1 650 cm^{-1}). Other heterocyclic imines such as 2-imino-1,3-thiazolidine-4,5-diones ($\nu_{C=N}$ 1 660—1 670 cm^{-1}) [9] and 5-imino-1,2,4-thiazolidine-3-thiones ($\nu_{C=N}$ 1 615—1 635 cm^{-1}),[10] and other examples [11] exhibit absorptions in the same region. An alternative adduct with thione structure is expected to give rise to absorption at lower frequency. Thus, 2,4,5-trimethyl-Δ^5-1,2,4-triazoline-3-thione absorbs at 1 577 cm^{-1},[12a] and

[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Progr. N.M.R. Spectroscopy*, 1969, **5**, 211.
[8] E. Elkik and C. Francesch, *Bull. Soc. chim. France*, 1969, **3**, 903.
[9] H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.*, 1965, **30**, 2781.
[10] M. Komatsu, Y. Ohshiro, K. Yasuda, S. Ichijima, and T. Agawa, *J. Org. Chem.*, 1974, **39**, 957; T. Kinoshita, S. Sato, and C. Tamura, *Bull. Chem. Soc. Japan*, 1976, **49**, 2236.
[11] H. Böshagen and W. Geiger, *Chem. Ber.*, 1976, **109**, 659; J. Goerdeler and J. Ulmen, *ibid.*, 1972, **105**, 1568; J. Goerdeler, W. Kunnes, and F. M. Panshiri, *ibid.*, 1976, **109**, 848.
[12] (*a*) U. Anthoni, C. Larsen, and P. H. Nielsen, *Acta Chem. Scand.*, 1969, **23**, 537; (*b*) K. A. Jensen and P. H. Nielsen, *ibid.*, 1966, **20**, 597.

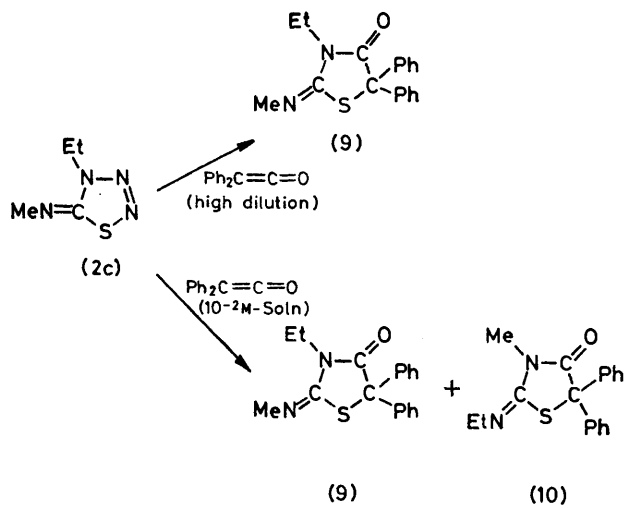
non-enolisable thioureas generally exhibit absorptions below *ca.* 1 500 cm^{-1}.[12b] Formation of (11) or (12) is in agreement with the results of L'abbé *et al.* who established this kind of structure for adducts of aminostyrenes and 5-benzyl-4-arylsulphonylaminothiatriazolines.[2]

(*b*) *Reaction with diphenylketen.* Rapid evolution of



SCHEME 2

nitrogen is observed on addition of diphenylketen to (2a) in CCl_4 at room temperature, and compound (8) is isolated in 44% yield (Scheme 2). The structure is inferred from independent synthesis of (8) from diphenylchloroacetic acid and 1,3-dimethylthiourea as depicted

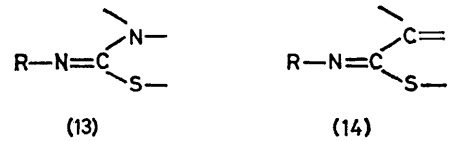


SCHEME 3

in Scheme 2. The reaction sequence with attack at sulphur is well established as a general method of preparation of similar thiazole derivatives.

Addition of diphenylketen to (2c) leads either to a single product or to an approximately 1 : 1 mixture of isomers. Thus (9) is formed exclusively in 64% yield under highly dilute reaction conditions, while a mixture of (9) and (10) is formed under more concentrated conditions ($\sim 10^{-2}$M) (Scheme 3). Compound (2b) behaves similarly giving rise to an approximately 1 : 1 mixture of (9) and (10). Attachment of ethyl and methyl groups to their respective positions in (9) and (10) was established by means of ^{13}C n.m.r. spectroscopy (see Experimental section).

A characteristic reaction of heterocycles of the type (13) and (14) to which the thiatriazolines (2) belong, is 1,3-dipolar cycloaddition with heterocumulenes across the imino-group and S(1), followed by extrusion of a fragment which in the present case would be nitrogen.[13] However, this ought to give only a single product (10) and not a mixture of (9) and (10). The cycloaddition products are thermally stable and do not undergo isomerization in solution at room temperature for 24 h



either with or without addition of thiatriazoline, carbodiimide, or diphenylketen. This problem is clearly in need of more detailed investigation.

EXPERIMENTAL

^1H N.m.r. spectra were obtained with Varian A-60A (60 MHz) and Bruker 270 MHz instruments ($CDCl_3$; $SiMe_4$ as internal standard). I.r. spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer and mass spectra on an AEI MS-902 instrument at 70 eV and 120 °C with a direct inlet system. Very weak absorptions have been omitted.

Reaction of Substituted 5-Amino-1,2,3,4-thiatriazoles with Trialkyloxonium Tetrafluoroborates.—Compound (3a). Equimolar amounts (0.1 mol) of (1; R = Me) and trimethyloxonium tetrafluoroborate were allowed to react in dry methylene chloride (800 ml) with stirring at 5 °C for 24 h. The solvent was removed under reduced pressure, the residue treated with absolute ethanol, and the precipitate filtered off, washed several times with ice-cold ethanol, and dried.

Compound (3b). This was prepared in the same manner and amount as compound (3a) from (1; R = Et). However, after evaporation of the solvent a semisolid material was obtained, which was treated with ethyl acetate and kept at 0 °C for 2—3 days to give crystalline material. This was filtered off and washed several times with ethyl acetate and absolute ethanol.

Compounds (3c) *and* (3d). Equimolar amounts of (1; R = Me) or (1; R = Et) (0.1 mol) and triethyloxonium tetrafluoroborate were allowed to react in methylene chloride (250 ml) at 5 °C for 24 h. Work-up was performed as for compound (3a).

[13] M. Baudy and A. Robert, *J.C.S. Chem. Comm.*, 1976, 912; K. Akiba, T. Tsuchiya, and N. Inamoto, *Tetrahedron Letters*, 1976, 1877; K. Akiba, M. Ochiumi, T. Tsuchiya, and N. Inamoto, *ibid.*, 1975, 459; J. E. Oliver and R. T. Brown, *J. Org. Chem.*, 1974, **39**, 2228 and references therein.

Compounds (3e) *and* (3f). Equimolar amounts (0.05 mol) of (1; R = Ph) and the trialkyloxonium tetrafluoroborate were allowed to react in dry methylene chloride (85 ml) with magnetic stirring at 5 °C for 3 days. The reaction product was filtered off and washed with methylene chloride. More material could be obtained on evaporation of the filtrate and digestion of the residue with chloroform.

Compound (2g). Equimolar amounts (10^{-3} mol) of (1; R = *p*-$MeC_6H_4SO_2$) and trimethyloxonium tetrafluoroborate were allowed to react in dry methylene chloride (20 ml) with magnetic stirring at room temperature for 24 h. The mixture was filtered and the solvent removed *in vacuo*. The oil obtained crystallized on digestion with ethanol, m.p. 116—118 °C. The n.m.r. spectra of the product were identical with those of compound (2g) obtained by Neidlein and Salzmann [3b] by the diazomethane method. For yields and m.p.s for compounds (3a—g), see Table 1. Elemental analysis (calc. values in parentheses) and i.r. data (KBr) are collected below: (3a) ν(C=N) 1 630 cm^{-1}, Found: C, 16.55; H, 3.35; N, 25.25; S, 15.25. Calc. for $C_3H_7N_4SBF_4$: C, 16.53; H, 3.24; N, 25.70; S, 14.71%; (3b) ν(C=N) 1 630 cm^{-1}, Found: C, 20.65; H, 3.85; N, 24.1; S, 13.7. Calc. for $C_4H_9N_4SBF_4$: C, 20.70; H, 3.91; N, 24.15; S, 13.82%; (3c) ν(C=N) 1 620 cm^{-1}, Found: C, 20.85; H, 3.85; N, 24.1; S, 13.85. Calc. for $C_4H_9N_4SBF_4$: C, 20.70; H, 3.91; N, 24.15; S, 13.82%; (3d) ν(C=N) 1 615 cm^{-1}, Found: C, 24.25; H, 4.7; N, 22.85; S, 12.9. Calc. for $C_5H_{11}N_4SBF_4$: C, 24.41; H, 4.51; N, 22.77; S, 13.03%; (3e) ν(C=N) 1 610 cm^{-1}, Found: C, 34.55; H, 3.35; N, 19.95; S, 11.2. Calc. for $C_8H_9N_4SBF_4$: C, 34.31; H, 3.24; N, 20.01; S, 11.45%; (3f) ν(C=N) 1 610 cm^{-1}, Found: C, 36.5; H, 3.85; N, 19.15; S, 11.1. Calc. for $C_9H_{11}N_4SBF_4$: C, 36.76; H, 3.77; N, 19.05; S, 10.90%.

Preparation of Thiatriazolines (2a—f) *from the Tetrafluoroborate Salts* (3a—f).—The tetrafluoroborate salt (3a—f) was dissolved in aqueous sodium hydrogen carbonate or hydroxide (3f) and extracted several times with methylene chloride or chloroform. The extract was dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Compounds (2a—d) were obtained as oils and (2e) and (2f) as solids, which were recrystallized from hexane and pentane respectively, m.p.s are given in Table 1 and n.m.r. data in Table 2. I.r. ($CHCl_3$), ν(C=N): (2a), 1 650; (2b), 1 645; (2c), 1 635; (2d), 1 640; (2e), 1 620; and (2f), 1 620 cm^{-1}.

5-(N-*Methyl*-p-*tolylsulphonylamino*)*thiatriazole* (4; R = *p*-$MeC_6H_4SO_2$).—The thiatriazole (1; R = Me; 10^{-2} mol) was dissolved in pyridine (15 ml) and toluene-*p*-sulphonyl chloride (10^{-2} mol) was added at room temperature with stirring. After 24 h pyridine was removed *in vacuo* and the oily residue taken up in acetone, filtered, and evaporated to dryness *in vacuo*. The product thus obtained was purified by preparative t.l.c. [Kieselgel, ether–light petroleum (1 : 1)] and finally recrystallized from benzene–light petroleum; it had m.p. 134 °C. The i.r. spectrum of this compound is superimposable on the i.r. spectrum of the compound obtained by Neidlein and Salzmann from reaction of 5-*p*-tolylsulphonylaminothiaztriazole with diazomethane and formulated as 5-(*N*-methyl-*p*-tolylsulphonylamino)thiatriazole (m.p. 130 °C).[3b]

Formation of 4-*Methyl*-5-p-*tolylsulphonylimino*-1,2,3,4-*thiatriazoline* (2g) *from Methyl Azide and Toluene*-p-*sulphonyl Isothiocyanate*.—Equimolar amounts (6×10^{-2} mol) of methyl azide and toluene-*p*-sulphonyl isothiocyanate in CCl_4 (15 ml) were allowed to react at 5 °C overnight. The solvent was removed *in vacuo* and the oily product treated with cyclohexane–light petroleum to give a crude product, which was recrystallized from CCl_4; m.p. 117—118 °C (decomp.); i.r. (KBr) ν(C=N) 1 530 cm^{-1}, mass spectrum, 270 ($M^{+\cdot}$, 6.4%), 210 ($M^{+\cdot} - N_2S$, 7.8%), 155 ($C_7H_7SO_2^+$, 36%), and 91 (100%).

Thermal Decomposition of the Thiatriazolines (2a—d).—Solutions (0.2 mol) of (2a—d) in dry 1,2-dichlorobenzene were heated in an oil-bath (125 °C) for 18—20 h under nitrogen. The yield of carbodi-imide obtained was determined by gas chromatography using electronic integration and comparison with calibration curves. Bromobenzene was added as internal standard after completion of the reaction; yields: (2b), 7%, (2c), 16%, and (2d), 52%.

Reactions of the Thiatriazolines (2a—c) *with Diphenylketen*.—Diphenylketen (7×10^{-3} mol) was added with stirring to a solution of compounds (2a—c) (6×10^{-3} mol) in CCl_4 kept at 25—30 °C by means of an ice-bath. After addition stirring was continued for 2 h at room temperature. The solvent was removed *in vacuo* and the residue treated with absolute ethanol to give one of the isomeric adducts, which was purified by recrystallization from acetone. The alcohol solution was worked up by means of preparative t.l.c. (ether–light petroleum 1 : 1) to give the other isomer together with a small amount of the first. From (2a) compound (8) was obtained in 44% yield; m.p. 115—116 °C; i.r. (KBr) 1 715 ν(C=O) and 1 650 cm^{-1} ν(C=N). Compound (2b) gave rise to a mixture of (9) and (10) in 23.7 and 29.7% and 21.3 and 26.5% yields respectively in two experiments. Compound (2c) gave rise to (9) and (10) in 26.6 and 14.5% and 25.4 and 10.6% yields respectively in two experiments. Compound (9) had m.p. 127—128 °C, i.r. (KBr) 1 720 ν(C=O) and 1 640 cm^{-1} ν(C=N). Compound (10) an oil, had i.r. ($CHCl_3$) 1 720 ν(C=O) and 1 640 ν(C=N). Mass spectra of (9) and (10): *m/e* (%) 310 (81, $M^{+\cdot}$), 295 (31, $M^{+\cdot} - CH_3$), 198 (100, $Ph_2CS^{+\cdot}$), 194 (48, $Ph_2C{=}CO^{+\cdot}$), 165 (88), 121 (60), and 91 (26).

Synthesis of 2-*Methylimino*-3-*methyl*-5,5-*diphenylthiazolidin*-4-*one*.—Equimolar amounts (0.01 mol) of *NN'*-dimethylthiourea and chlorodiphenylacetic acid were refluxed with anhydrous sodium acetate (0.015 mol) in glacial acetic acid (15 ml) for 4 h. The reaction mixture was poured into ice-water and the resulting crystalline product collected by filtration was washed several times with water, dried, and recrystallized from acetone; it had m.p. 115—116 °C. The i.r. spectrum was identical with that of the adduct of (2a) and diphenylketen.

Reactions of Thiatriazolines (2a—c) *with* β-NN-*Dimethylaminostyrene*.—Compound (2) (3×10^{-2} mol) was added to neat β-*NN*-dimethylaminostyrene (1 ml) and kept at 40 °C for 22 h. Evolution of nitrogen was observed immediately. The reaction mixture was worked up by preparative t.l.c. (alumina, light petroleum–acetone, 4 : 1) to give an oily product, which was purified by short-path distillation at 80 °C and 0.1 mmHg; (2a) + enamine: n.m.r. (CCl_4): δ 2.27 (NMe_2), 2.85 (NMe), 2.98 (NMe); CH–CH ν_A = δ 4.39 and ν_B = δ 4.26 (J = 2.3 Hz); i.r. ($CHCl_3$) ν(C=N) 1 635 cm^{-1}; mass spectrum: 249 ($M^{+\cdot}$, 25%), 205 ($M^{+\cdot} - NMe_2$, 76%), 204 ($M^{+\cdot} - HNMe_2$), 53%), 147 (aminostyrene, 53%), 146 (25%), 132 (*m/e* 205 — CH_3NCS, 100%), 122 (34%), 121 (20%), 117 (23%), 91 (49%), and 86 (35%).

(2b) or (2c) + *enamine*: mass spectrum, 263 ($M^{+\cdot}$ 8.1%), 219 ($M^{+\cdot} - NMe_2$, 42%), 218 ($M^{+\cdot} - HNMe_2$, 34%), 147 (aminostyrene, 100%), 146 (58%), 132 (38%), 84 (38%), and 69 (73%); yield 54%; i.r. ($CHCl_3$), ν(C=N) 1 640 cm^{-1}; n.m.r. (CCl_4): δ 2.27 (NMe_2), 2.85 (NMe), 2.98 (NMe),

3.16 and 1.09 (NEt), 3.14 and 1.16 (NEt) (J = 7.05 Hz, 7.13 Hz).

5-Dialkylaminothiatriazoles.— 5-Dimethylaminothiatriazole was prepared according to a literature method.[14] 5-Diethylaminothiatriazole, hitherto unknown, was prepared similarly from 4,4-diethylthiosemicarbazide and HNO_2: it had m.p. −5 °C (Found: C, 38.05; H, 6.15; N, 35.65; S, 20.37. Calc. for $C_5H_{10}N_4S$: C, 37.95; H, 6.37; N, 35.41; S, 20.27%).

^{13}C N.m.r. Spectroscopy of Cycloaddition Products (8)—(10).—^{13}C Proton-decoupled spectra of the cycloaddition products from diphenylketen and thiatriazolines (2a) [to give (8)] and (2d) gave the following chemical shift values (p.p.m., $CDCl_3$, $SiMe_4$) respectively: 29.83 (MeN=), 38.54 (MeN), and 38.34 (CH_3CH_2N=), 12.61 (CH_3CH_2N=), 46.92 (CH_3CH_2N), and 15.86 (CH_3CH_2N). Compounds (9) and (10) obtained from (2b) or (2c) gave the following chemical shift values: (9), 30.02 (CH_3N=), 46.92 (CH_3CH_2N), and 15.92 (CH_3CH_3N); (10), 38.73 (CH_3N), 38.47 (CH_3CH_2N=), and 12.73 (CH_2CH_2N=). Assignments of the respective methyl and ethyl groups in the cycloaddition products are based on comparison with different methyl and ethyl substituted amines, amides, hydrazides, and carbamates: *NN*-dimethyl-t-butylamine (38.74),[15] *NN*-dimethyl-s-butylamine (40.60),[15] 1-methylacetylhydrazide (37.8 and 38.7),[16] *NN*-diethyl-s-butylamine [43.44 (CH_2) and 15.12 (CH_3)],[15] ethyl *NN*-diethyldithiocarbamate [49.2, 46.7 (CH_2), 12.4, and 11.7 (CH_3)],[16] *NN*-dimethylacetamide (34.5 and 37.5),[17] and *NN*-dimethylformamide (36.2 and 31.1).[17]

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[14] K. A. Jensen and C. Pedersen, *Adv. Heterocyclic Chem.*, 1964, **3**, 263.
[15] H. Eggert and C. Djerassi, *J. Amer. Chem. Soc.*, 1973, **95**, 3710.
[16] H. Eggert, personal communication.
[17] L. F. Johnson and W. C. Jankowski, ' Carbon-13 N.M.R. Spectra,' John Wiley, New York, 1972.