Methyltropic Tautomerism of the N–C–O and N–C–S Groups: Synthesis of Methyl Mono- and Di-thiocyanurates

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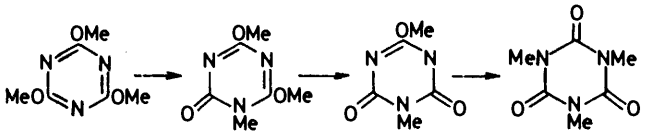
A number of well defined trimethyl mono- and di-thiocyanurates have been synthesised following a procedure which consists of two reactions, (i) nucleophilic substitution of an SMe group, bound to a substituted *s*-triazine ring, with an OMe group; and (ii) the thermal isomerisation of the product of reaction (i). Two reaction sequences are described whose starting compounds are respectively the unsymmetric *S,N,N*-(1) and *S,S,N*-trimethyl trithiocyanurates (9). The corresponding dimethyl esters were obtained upon hydrolysis of the products of reaction (i).

Four trimethyl and two dimethyl dithiocyanurates; and four trimethyl and two dimethyl monothiocyanurates have been obtained and characterised; ten of them are reported for the first time.

The rules of methyl migration in the thermal isomerisation, established in previous works, are confirmed and extended.

In previous studies of methyl cyanurates their thermal isomerisation has been shown[1] to be a stepwise process (see Scheme 1). This may be written symbolically as



Scheme 1

shown in equation (1) where O and N are the atoms to which the methyl groups are bound.

$$O.O.O \longrightarrow O.O.N \longrightarrow O.N.N \longrightarrow N.N.N_{(O)} \quad (1)$$

It was later shown that the methyl thiocyanurates undergo a similar stepwise, but reverse, thermal isomerisation process,[2] [see equation (1′)].

$$N.N.N_{(S)} \longrightarrow S.N.N \longrightarrow S.S.N \longrightarrow S.S.S \quad (1')$$

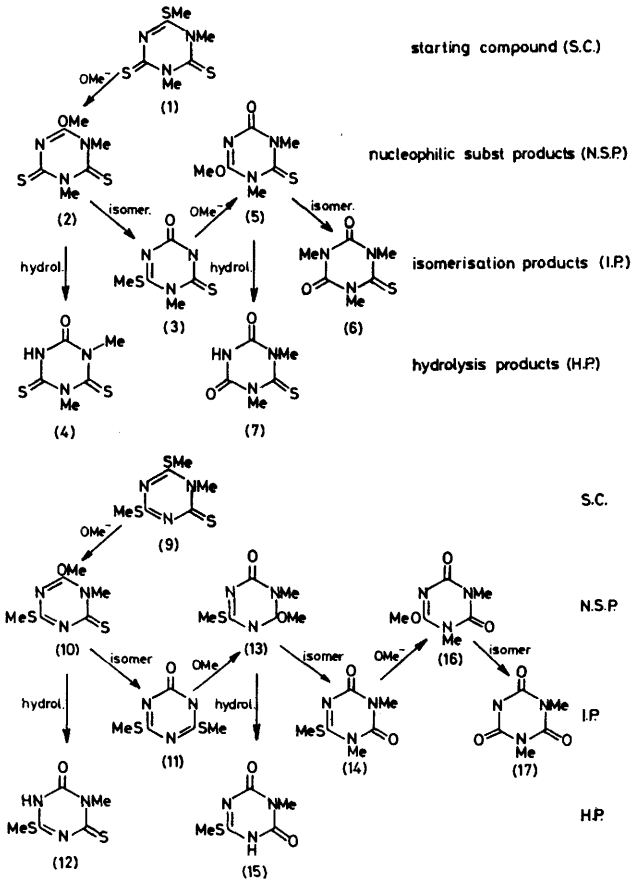
An important step towards an understanding of the isomerisation mechanism was the synthesis of the unsymmetrically substituted esters (O.O.N, *etc.*):[3,4,5] for example, it was not possible to obtain the intermediate unsymmetric esters O.O.N and O.N.N from the thermal isomerisation of the O.O.O compound [see equation (1)],[6,7] the product always being of the $N.N.N_{(O)}$ type. The absence of these compounds was a result of their marked thermal instability: in fact, it was shown that they undergo isomerisation to $N.N.N_{(O)}$ even in the solid state at temperatures below the onset of O.O.O isomerisation.

From previous work [1,5] it is possible to summarise the reaction characteristics as follows. (i) Processes (1) and (1′) are reversible; (ii) the thermal stability of the symmetrically substituted esters is greater than that of the corresponding unsymmetrical esters; (iii) the thermal stability of the O-unsymmetric esters is less than that of the S-unsymmetric esters (whose melts isomerise at temperatures higher than 200 °C).

Since this tautomeric isomerisation differs from that for other oxygen- and sulphur-substituted aza-aromatic compounds the thermal behaviour of compounds possessing both NCO and the NCS groups in the same molecule was investigated. Only the trimethyldithiocyanuric acid, N.N.N,[8] and the trimethylmonothiocyanuric acid, N.N.N,[9] have been reported in the literature, but the synthetic route described was of no help in the present case. A new procedure for the preparation of mono- and di-thiocyanurates has, therefore, been investigated.

RESULTS

Synthetic Procedure.—Trimethyl mono- and di-thiocyanurates have been prepared from (1), S.N.N, and (9), S.S.N, by the following procedure: nucleophilic substitution of methanethiolate by methoxide in methanol [10] and thermal



Scheme 2

isomerisation of the substitution products. The latter consisted of heating the solid substitution products which resulted in the migration of one methyl group from the oxygen to a sulphur or nitrogen atom. For structural identification purposes a hydrolytic reaction was carried out on each product obtained from the *S*-methyl ⟶ *O*-methyl substitution reaction to give the corresponding dimethyl esters.

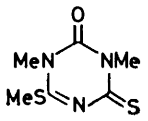
The results are summarised in Scheme 2.

The thermal isomerisations of the nucleophilic substitution products may all take place in the solid phase and for some [*e.g.* (2) ⟶ (3) and (10) ⟶ (11)] at room temperature. As a consequence, melting point determination of these products is impossible because all melts are mixtures of two isomers whose ratio depends on the rate of heating. Only (5), when very quickly brought to fusion, shows just trace amounts of its isomer (6). The isomerisations go to completion and side products are absent. The isomers are thermally stable since there is no transformation when they are heated at 200 °C for 30 min.

Hydrolyses, achieved by passage of HCl through a methanolic solution, were complete in a few minutes at room temperature.

Structure Identification.—The products were generally identifiable by use of n.m.r. spectroscopy and reference to the starting materials. Only compounds (3), (10), and (13) were exceptions since alternative structures were possible in each case. All rejected alternatives have been labelled in the Discussion section and Schemes by use of a prime on the numbers of the corresponding correct structure.

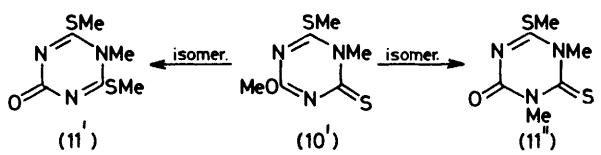
Compound (3). Although this compound could have the alternative structure (3′), its nucleophilic substitution



(3′)

product (5) undergoes hydrolysis to (7) whose n.m.r. spectrum shows a single resonance peak corresponding to two equivalent methyl groups: a hydrolysis product originating from (3′) (after nucleophilic substitution of its SMe group with an OMe group) would have two n.m.r. peaks corresponding to the two non-equivalent methyl groups; structure (3′) may, therefore, be discounted.

Compound (10). The nucleophilic substitution from which this compound originates could take place at the alternative SMe group of (9), and give the alternative structure (10′); both (10) and (10′) are structures consistent with the observed n.m.r. spectrum, but structure (10′) may be discounted since its possible isomerisation products (11′) and (11″) have structures inconsistent with the n.m.r. spectrum of the product obtained: (i) three peaks of equal intensity are inconsistent with structure (11′) and (ii) the two peaks at 2.50 and 2.59 p.p.m. are unambiguously assigned to SMe groups thus ruling out structure (11″).



(11′) (10′) (11″)

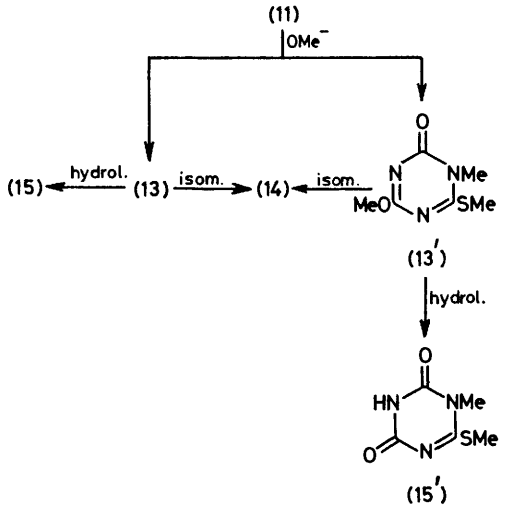
SCHEME 3

Compound (13). A different approach has to be used to distinguish between (13) and (13′), the two possible products from (11), since both give the same isomerisation product (14).

Although (13) and (13′) give different hydrolysis products, (15) and (15′), and different isomerisation products (not shown in Scheme 4) when the migrating methyl group is labelled, the differences in structure are not such as to allow a distinction to be made between the relative positions of the NMe and SMe_3 groups from the n.m.r. spectra.

However, by comparing the n.m.r. spectrum of the product with those of other products whose structures have been established a distinction between compounds (13) and (13′) was possible. Inspection of the n.m.r. signals plotted in the Figure shows that there is a clearly identifiable range for the NMe groups in relation to the nature of the adjacent groups (see also the Table).

The question of whether (13) or (13′) is the structure of the product obtained is thus reduced to identifying the groups



SCHEME 4

adjacent to the NMe; the answer to this then comes from the signal at 3.37 p.p.m. Since it falls in the ' d ' range it is clear that the product has structure (13), in which both

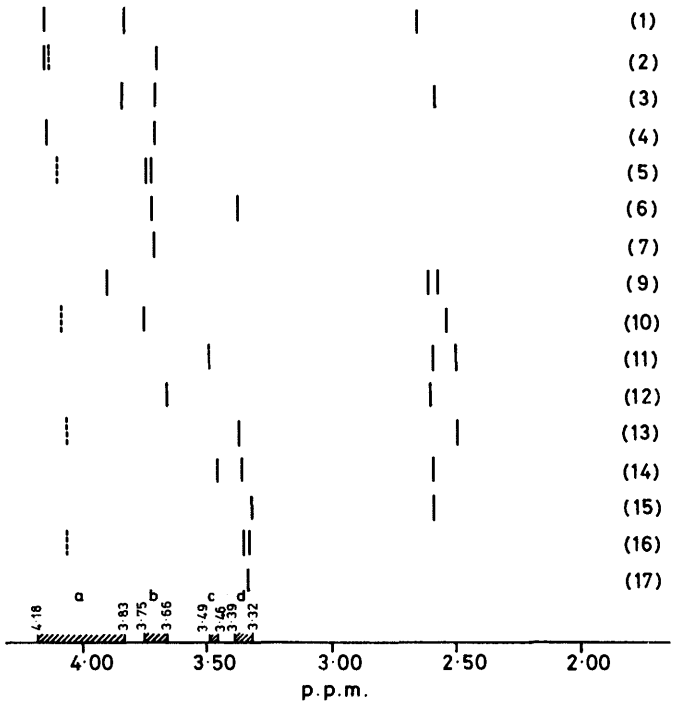
NMe ^{1}H N.m.r. absorption ranges in relation to adjacent groups

Signal ranges (p.p.m.)	R and R′ groups adjacent to NMe (RC·NMe·CR′)	Compounds *
' a ' 4.18—3.83	R = S; R′ = S or SMe	(1), (2), (3), (9), N.N.N [a]
' b ' 3.75—3.66	R = S; R′ = O or OMe	(2), (3), (4), (5), (6), (8), (10), (12)
' c ' 3.49—3.46	R = O; R′ = SMe	(11), (14)
' d ' 3.39—3.32	R = O; R′ = O or OMe	(6), (14), (15), (16), (17), O.O.N [b]

* The NMe peaks of hexahydro-1,3,5-trimethyl-2,6-dithioxo-1,3,5-triazine-4-one [12] fit into this scheme. They are at 4.17 p.p.m. for N(1)–Me (whose adjacent groups are R = R′ = S), and 3.72 p.p.m. for the two equivalent N(3)–Me and N(5)–Me (R = S, R′ = O).

[a] Hexahydro-1,3,5-trimethyl-1,3,5-triazine-2,4,6-trithione: the peak of its three equivalent NMe groups (R = R′ = S) is at 4.18 p.p.m. [b] Dihydro-4,6-dimethoxy-3-methyl-1,3,5-triazin-2-one: the peak of its NMe group (R = O; R′ = OMe) is at 3.39 p.p.m.

positions adjacent to the NMe are *O*-substituted. Further proof of this is to be found in the n.m.r. spectrum of the hydrolysis product (15), the peak at 3.32 p.p.m. of which indicates an NMe group that again has *O*-substitution on both adjacent positions. The NMe signal of (15′) should have fallen in the range ' c ' of the Table.



^{1}H(Me) N.m.r. spectra in $CDCl_3$ ($SiMe_4$ as internal reference) of the listed compounds. The ranges ' a ' and ' c ' are extended beyond the limits defined by the above compounds in order to include the NMe peaks of the *N,N,N*- and *O,O,N*-trimethylcyanurates reported in the Table

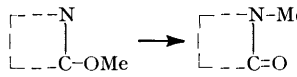
DISCUSSION

The procedure described led us to obtain four of the ten * possible trimethyl mono- and di-thiocyanurates. The reason for this is to be found in the remarkable specificity of the nucleophilic substitution and isomerisation reactions reported in the foregoing.

All observed nucleophilic substitutions took place at the carbon atom interposed between nitrogen atoms of different valence state: N(tr^2, tr^1, tr^1, π^1, V_2) and N(tr^1, tr^1, tr^1, π^2, V_3).† The SMe groups bound to carbon atoms lying between nitrogen atoms of the same valence state, (9) and (11), do not undergo substitution; the experimental results obtained in the methanolysis of the 1,2,4-triazine derivatives [10,11] are in line with this observation.

All observed isomerisations can occur in the solid, and a common feature is removal of Me from OMe. The end products are of two kinds: either the result of methyl transfer to sulphur, which take place at room temperature; or, when no thione group is available, the methyl group migrates to a ring nitrogen at *ca.* 80 °C.

S=(Etherocyclic)-O-Me ⟶ Me-S-(Etherocyclic)=O (2)



(3)

Reaction (2) needs some comment with reference to the valence state of the atoms involved. With reference to equations (1) and (1′) the isomerisations of the methoxytriazines are lactim ⟶ lactam processes with methyl transfer from oxygen to nitrogen connected with the following valence-state changes:

$$O(tc^2,te^2,te^1,te^1,C_2) \longrightarrow O(tr^2,tr^2,tr^1,\pi^1,V_1)$$
$$N(tr^2,tr^1,tr^1,\pi^1,V_2) \longrightarrow N(tr^1,tr^1,tr^1,\pi^2,V_3) \quad (3a)$$

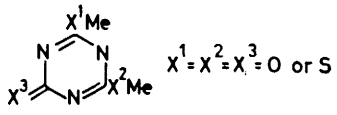
The isomerisations of the *N*-methyltrithiocyanuric acids are thiolactam ⟶ thiolactim processes with valence-state changes

$$S(tr^2,tr^2,tr^1,\pi^1,V_1) \longrightarrow S(te^2,te^2,te^1,te^1,V_2)$$
$$N(tr^1,tr^1,tr^1,\pi^2,V_3) \longrightarrow N(tr^2,tr^1,tr^1,\pi^1,V_2) \quad (4)$$

The starting compound of reaction (2) does not react according to equations (3a), although this could, in principle, occur. The observed course is actually a combination of equations (3a) and (4): in practice the thermal isomerisations of compounds (2) and (10) bring about a combined valence-state change of oxygen and sulphur. Thus reaction (2) could be the result of a two-step process, *i.e.* (3a) followed by (4). This is not, however, the case since, first, reaction (2) takes place at room temperature whereas reaction (4) has never been observed at temperatures lower than 200 °C, and, secondly, if, for example, (2) ⟶ (3) were a two-step reaction, the n.m.r. spectrum of the isomerisation product obtained from the labelled compound (2) should show the SMe signal even if reduced to 50% for obvious statistical reasons (Scheme 5). The reaction product does not show the SMe signal thus proving that there is no N–CD_3 intermediate.

Previous studies on the mechanism of the thermal isomerisation,[1] carried out in the melt at 180 °C, assumed as the first step of the process the ionic dissociation of

* This number of possible isomers can be reduced to eight if, by analogy with the trimethyl cyanurate and trithiocyanurates for which compounds like (8) have never been obtained, it is



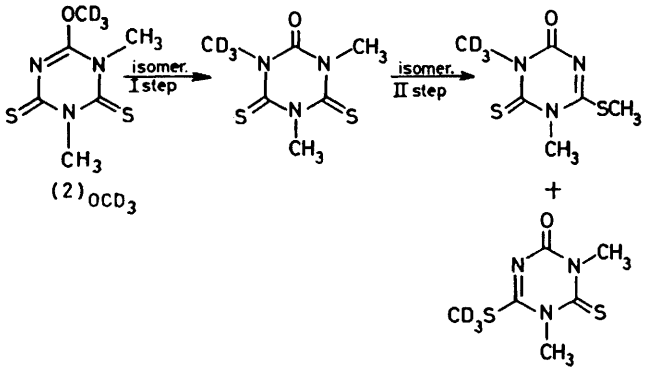
(8)

assumed that three adjacent methyl groups probably confer to these structures such a thermal instability that they do not practically exist under normal conditions.

† The meaning of this Mulliken notation is described in R. S. Mulliken, *J. Chem. Phys.*, 1951, **19**, 900 and references therein. It gives the valence electron assignment among the available hybrid atomic orbitals, tr, te, π standing for trigonal, tetrahedral, and 2*p*, respectively. The subfix *n* in V_n gives the number of atoms adjacent to the one considered: *e.g.* N(tr^2, tr^1, tr^1, π^1, V_2) correspond to the valence state of nitrogen in pyridine and similar compounds.

the neutral molecule and considered the Me^+ cation as the active species. This was also in agreement with solid-state isomerisations reported. The present results fit into the proposed mechanism * whereas alternative mechanisms cannot account for the solid-state reactions.

Experimental results obtained in this study of molecular structures containing both the NCS and the NCO systems allow some conclusion to be drawn. Their tendency to thermal isomerisation appears enhanced with respect to structures made up by only one of the two systems exhibiting methyl-tropic tautomerism, *i.e.* trimethyl cyanurates or trithiocyanurates. Maximum thermal instability appears whenever NCO and NCS are combined in such a way that a methoxy and a thione group, accessible to methyl attack, are present together [*e.g.* compounds (2) and (10)].



SCHEME 5

In conclusion, the results obtained on these and on previously studied methyltropic systems show that the isomerisation goes in the direction that allows the formation of structures that contain the maximum number of thiolactim $-N{=}C{-}SCH_3$ and lactam $CH_3{-}N{-}C{=}O$ groups.

EXPERIMENTAL

Nucleophilic Substitutions.—Sodium methoxide concentration must be controlled in order to avoid hydrolysis products, and, generally, must not exceed a molar ratio of 1 : 10 with respect to substrate concentration. Under reflux the reactions are complete in a few minutes; no side-product is formed.

Isomerisation Reactions.—These were carried out using a Buchi m.p. apparatus. Reaction mixture compositions were tested by means of t.l.c. carried out with 0.25-mm thick silica-gel pre-coated plates with fluorescent indicator (C. Erba). The R_F values reported were determined by elution with a 2% methanol in $CHCl_3$ solution. All examined compounds appear as fluorescent spots except the cyanuric acid derivatives (16) and (17). I.r. spectra were recorded with a Perkin-Elmer spectrometer for solutions in $CHCl_3$ (0.1-mm thickness), unless otherwise stated. N.m.r. spectra were recorded with a Varian XL100 instrument for solutions in $CDCl_3$ using $SiMe_4$ as internal reference. Absorption frequencies are given in p.p.m. with respect to $SiMe_4$ those of the acidic protons of the hydrolysis products are not reported: they appear as flat peaks, usually beyond 9 p.p.m., and their positions are concentration dependent.

Mass spectra were recorded with an LKB Gas-Chromatograph–Mass Spectrometer by direct inlet technique (40—60 °C; E.E. 20 eV).

Elemental analysis were performed by the Microanalysis Service of these Laboratories under the direction of Dr. A. Mazzeo.

Tetrahydro-4-methoxy-1,3-dimethyl-1,3,5-triazine-2,6-dithione (2).—This compound was obtained quantitatively by refluxing a methanol solution of (1) (1 mmol) in solvent (100 ml) together with MeONa (0.02 mmol). Higher methoxide concentrations caused formation of the hydrolysis product (4). In the absence of sodium methoxide, (2) was obtained at a much slower rate (*ca.* 40 days at room temperature). It is stable in $CHCl_3$ solution; in the solid state at room temperature it underwent isomerisation to (3): after 30 min at 28 °C transformation was *ca.* 50%; δ 3.70 (3 H, 3-Me), 4.13 (3 H, 1-Me), and 4.15 (3 H, OMe). The last assignment was done on the basis of the disappearence of this signal when compound (2) was obtained in [$^2H_4$]-methanol solution.

Elemental analysis was performed on the isomerisation product (3), R_F 0.62 [compound (1) R_F 0.65].

Tetrahydro-1,3-dimethyl-6-methylthio-2-thioxo-1,3,5-triazin-4-one (3).—This compound was obtained by spontaneous isomerisation of compound (2) at room temperature; it formed white needles from water, m.p. 172—173 °C. (Found: C, 35.45; H, 4.55; N, 20.8; S, 31.6; Calc. for $C_6H_9N_3OS_2$: C, 35.47; H, 4.43; N, 20.69; S, 31.53%); δ 2.59 (3 N, SMe), 3.71 (3 H, 3-Me), 3.84 (3 H, 1-Me); i.r.; 1 700s, 1 560s, 1 380s, 1 125m, and 1 055m cm^{-1}; M^+, *m/e* 203; R_F 0.59.

Hexahydro-1,3-dimethyl-2,6-thioxo-1,3,5-triazin-4-one (4).—This compound was prepared by dissolving compound (2) in acidic methanol and recovering the hydrolysis product by solvent evaporation; it was obtained as a white powder from water or ethanol, m.p. 172—173 °C (Found: C, 31.95; H, 3.75; N, 22.05. Calc. for $C_5H_7N_3OS_2$: C, 31.75; H, 3.70; N, 22.22%); δ 3.71 (3 H, 3-Me) and 4.14 (3 H, 1-Me); i.r.: 3 400w, 1 730s, 1 470s, 1 430m, 1 410s, 1 300m, and 1 080 cm^{-1}; M^+, 189; R_F 0.50.

Tetrahydro-6-methoxy-1,3-dimethyl-2-thioxo-1,3,5-triazin-4-one (5).—This compound was obtained by refluxing for a few minutes a methanolic solution of (3) (1 mmol in 100 ml of solvent) with NaOMe (0.1 mmol); it was obtained as white crystals from water; m.p. not recorded since isomerisation of the compound to (6) starts in the solid; when the temperature was raised rapidly the melt formed at 112—114 °C and contained only a trace amount of the isomer (6).

Slow formation of compound (5) from (3) was also observed in pure methanol (*ca.* 30% transformation in 40 days) (Found: C, 38.7; H, 4.9; N, 22.3. Calc. for $C_6H_9N_3O_2S$: C, 38.50; H, 4.85; N, 22.45%); δ 3.72 (3 H, NMe), 3.74 (3 H, NMe), and 4.10 (3 H, OMe); i.r.: 1 700m, 1 600s, 1 470s, 1 415m, 1 390s, 1 310m, and 1 105m cm^{-1}; M^+, *m/e* 187; R_F 0.55.

* The author is aware that many would discount the involvement of methyl cations in a rearrangement process. As the holder of a minority view however the author has chosen to remark simply that the present results fit into the previously proposed mechanism. Evidence in favour of a methyl cation mechanism has been recently obtained [13] in a correlation study of the influence of solvents on the rate of isotopic exchange of iodine in MeI.

Hexahydro-1,3,5-trimethyl-2-thioxo-1,3,5-triazine-4,6-dione (6).—This compound was produced quantitatively from (5) when kept for 20 min at 120 °C; it formed white crystals from water or ethanol, m.p. 149—150 °C (Found: C, 38.7; H, 4.9; N, 22.2. Calc. for $C_6H_9N_3O_2S$: C, 38.50; H, 4.85; N, 22.45%); δ 3.38 (3 H, 5-Me) and 3.72 (6 H, 1- and 3-Me); i.r.: 1 700m, 1 690s, 1 475s, 1 420m, 1 390m, 1 320m, and 1 310m cm^{-1}; M^+, *m/e* 187; R_F 0.67.

Hexahydro-1,3-dimethyl-2-thioxo-1,3,5-triazine-4,6-dione (7).—This compound, the hydrolysis product obtained from an acidic methanol solution of (5) after solvent evaporation, was a white powder, m.p. 189—191 °C (from water) (Found: C, 34.85; H, 4.15; N, 24.65. Calc. for $C_5H_7N_3O_2S$: C, 34.68; H, 4.08; N, 24.27%); δ 3.71 (6 H, 1- and 3-Me); i.r.: 3 400w, 1 720s, 1 470s, 1 415s, 1 370m, 1 305m, and 1 120m cm^{-1}; M^+, *m/e* 173; R_F 0.29.

Dihydro-4-methoxy-3-methyl-6-methylthio-1,3,5-triazine-2-thione (10).—This compound was produced upon heating a methanol solution of (9) (1 mmol in 100 ml solvent) under reflux with MeONa (0.1 mmol). It crystallised from a 10% ethanol–hexane mixture; its m.p. was ill-defined, the melt forming at *ca.* 130 °C, containing a large amount of the isomer (11). The pale yellow solid was unstable at room temperature and after *ca.* 20 days 50% of it was converted into (11) (Found: C, 35.6; H, 4.5; N, 20.6. Calc. for $C_6H_9N_3OS_2$: C, 35.45; H, 4.45; N, 20.6%); δ 2.54 (3 H, SMe), 3.75 (3 H, 3-Me), and 4.08 (3 H, OMe); i.r.: 1 508s, 1 510s, 1 500s, 1 432m, 1 412m, 1 360w, 1 340w, 1 280s, 1 135s, 1 075m, 1 020w, and 922w cm^{-1}; R_F 0.59 [$R_{N(11)}$ 0.62].

Dihydro-3-methyl-2,6-bismethylthio-1,3,5-triazin-4-one (11).—This compound was obtained by thermal isomerisation of (10), a process which is quantitative after 5 min at 150 °C; white crystals were obtained from water, m.p. 161—163 °C (Found: C, 35.6; H, 4.55; N, 20.55. Calc. for $C_6H_9N_3OS_2$: C, 35.45; H, 4.45; N, 20.7%); δ 2.50 (3 H, SMe), 2.59 (3 H, SMe), and 3.49 (3 H, 3-Me); i.r.: 1 692s, 1 465s, 1 412m, 1 272s, and 1 100w cm^{-1}; R_F 0.50.

Tetrahydro-3-methyl-6-methylthio-2-thioxo-1,3,5-triazin-4-one (12).—This compound was obtained upon hydrolysis of (10) dissolved in acidic methanol at room temperature. The product was recovered by solvent evaporation. It was also obtained, upon refluxing an aqueous solution of (10), as a white powder from water, m.p. 208—210 °C (Found: C, 31.9; H, 3.9; N, 22.05. Calc. for $C_5H_7N_3OS_2$: C, 31.75; H, 3.7; N, 22.2%); δ 2.60 (3 H, SMe) and 3.66 (3-H, 3-Me); i.r.: 3 390w, 1 710s, 1 570s, 1 500s, 1 430m, 1 370m, 1 280m, 1 125m, 990m, and 965w cm^{-1}; R_F 0.18.

Dihydro-2-methoxy-3-methyl-6-methylthio-1,3,5-triazin-4-one (13).—This compound was obtained upon refluxing a methanol solution of (11) (1 mmol in 100 ml solvent) added with MeONa (0.1 mmol). After the solution had been refluxed for few minutes the product was recovered by solvent evaporation and extraction with chloroform. The white residue was crystallised from a mixture of 10% ethanol in hexane; its m.p. was ill-defined, the melt forming at *ca.* 110 °C, containing a mixture of (13) and its isomer (14) which start to form in the solid state. Isomerisation was not observed at room temperature (Found: C, 38.6; H, 4.75; N, 22.15. Calc. for $C_6H_9N_3O_2S$: C, 38.5; H, 4.85; N, 22.45%); δ 2.50 (3 H, SMe), 3.37 (3 H, 3-Me), and 4.06 (3 H, OMe); i.r.: 1 680s, 1 585s, 1 505s, 1 445m, 1 408m, 1 325m, 1 300m, and 1 190m cm^{-1}; R_F 0.46.

Tetrahydro-1,3-dimethyl-6-methylthio-1,3,5-triazine-2,4-dione (14).—This compound was the thermal isomerisation product of (13). At 130 °C transformation was quantitative after 5 min. The white product was purified by sublimation: it had m.p. 131—133 °C (Found: C, 38.65; H, 4.85; N, 22.15. Calc. for $C_6H_9N_3O_2S$: C, 38.50; H, 4.85; N, 22.45%); δ 2.59 (3 H, SMe), 3.36 (3 H, 3-Me), and 3.46 (3 H, 1-Me); i.r.: 1 718m, 1 668s, 1 570s, 1 420m, 1 373m, and 1 175w cm^{-1}; R_F 0.48.

When compound (14), dissolved in methanol, was treated with small quantities of sodium methoxide it gave, under reflux, the *O,N,N*-trimethyl cyanurate (tetrahydro-6-methoxy-1,3-dimethyl-1,3,5-triazine-2,4-dione) (16), which was identified by comparison with an authentic sample.[4] In turn, this compound underwent thermal isomerisation to (17) (hexahydro-1,3,5-trimethyl-1,3,5-triazine-2,4,6-trione) which is the *N,N,N*-trimethyl cyanurate.[4]

Tetrahydro-3-methyl-6-methylthio-1,3,5-triazine-2,4-dione (15).—This compound was obtained by dissolving (13) in cold, acidic methanol. The hydrolysis product was recovered upon solvent evaporation. It was also obtained upon refluxing an aqueous solution of (13). It was purified by sublimation and melted with decomposition at *ca.* 230 °C; δ 2.59 (3 H, SMe_3) and 3.32 (3 H, 3-Me); i.r. (0.5 mm): 3 390w, 1 735s, 1 690s, and 1 580s cm^{-1}; R_F 0.09; M^+, *m/e* 173.

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