Cyclization of Isothiosemicarbazones. Part 7.[1] Synthesis of *N*-Alkenyl-1,2,4-triazoles with Anti-Saytzeff Orientation

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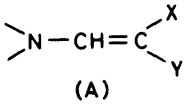
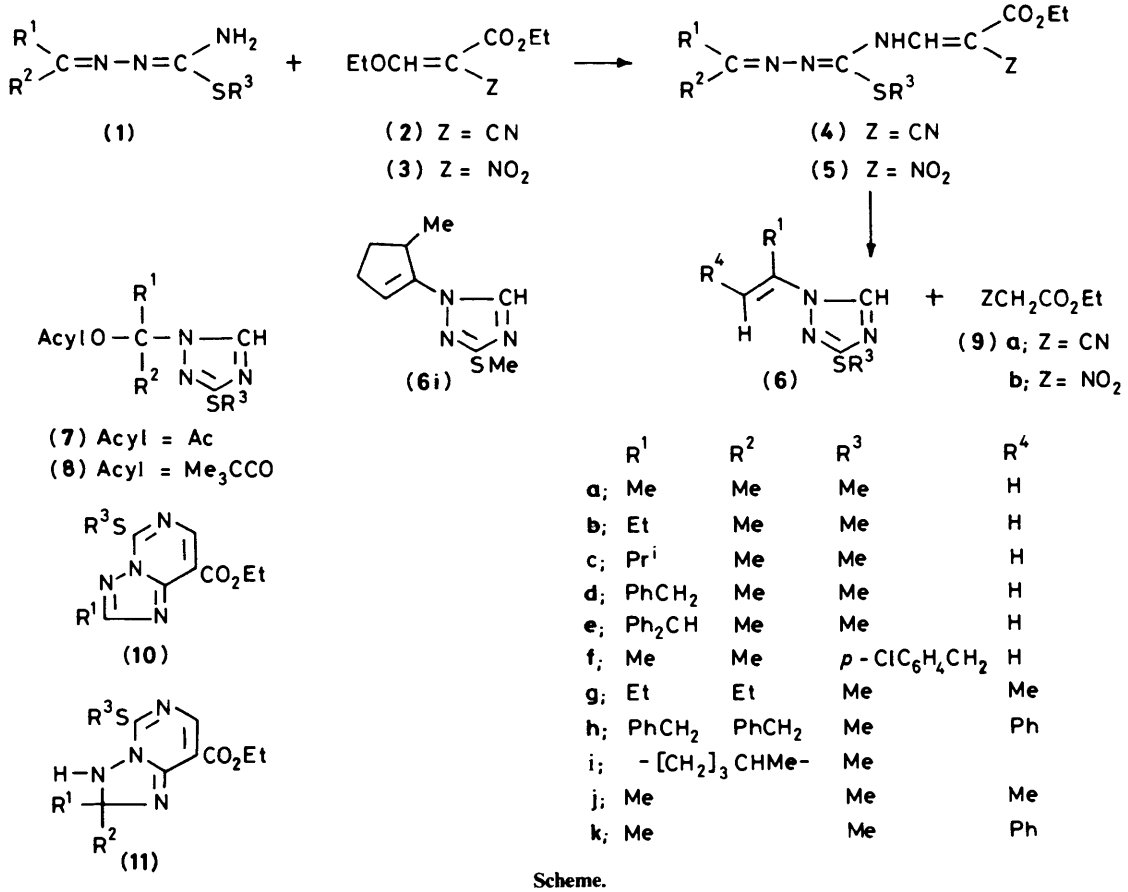
Aliphatic ketone 4-[2-cyano-2-(ethoxycarbonyl)vinyl]-3-methylisothiosemicarbazones (**4**) give *N*-alkenyl-1,2,4-triazoles (**6**) in moderate yields with elimination of ethyl cyanoacetate in hot acetic acid. When the carbonyl component is an unsymmetrical ketone, the reaction proceeds predominantly to afford the less substituted terminal alkenes, and little or no formation of the more substituted internal alkenes was observed, even though the internal alkene would be thermodynamically more favourable. Without an intervening isolation of the *N*(4)-(substituted vinyl) isothiosemicarbazones, these alkenes are obtained in much higher yields through a direct 'cycloalkenylation' of *N*(4)-unsubstituted isothiosemicarbazones (**1**) with ethyl β-ethoxy-α-nitroacrylate (**3**) along with a minor amount of 2(3)-(3-alkylthio-1,2,4-triazol-1-yl)alkan-2(3)-yl acetates (**7**). The proposed mechanism involves preferential abstraction of a proton at the less crowded alpha-carbon of the potentially formed iminium ion.

A general system of an electron-deficient ethylenic linkage (A),



(A)

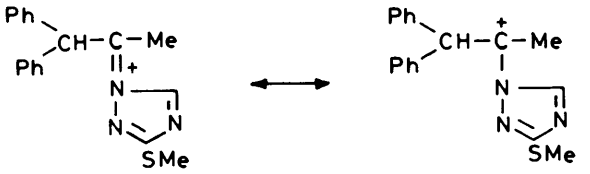
in which X and Y are each an electron-withdrawing group, may be attacked intramolecularly by sulphur-[2] or nitrogen-[3] nucleophilic centres to form heterocycles with elimination of CH_2XY in neutral-to-basic medium. In the previous paper,[1] we reported that alkanophenone 4-[2,2-bis(ethoxycarbonyl)-vinyl]-3-methylisothiosemicarbazones and *ortho*-substituted acetophenone 4-[2-cyano-2-(ethoxycarbonyl)vinyl]-3-methyl-isothiosemicarbazones (**4**; R^1 = *ortho*-substituted phenyl, R^2 = R^3 = Me) cyclized to 1-aryl-1-(3-methylthio-1*H*-1,2,4-triazol-1-yl)alkenes (**6**; R^1 = aryl) in acetic acid with elimination of diethyl malonate and ethyl cyanoacetate, respectively. It was also suggested that an acetaldehyde *N*(4)-(substituted vinyl)-



	R^1	R^2	R^3	R^4
a;	Me	Me	Me	H
b;	Et	Me	Me	H
c;	Pr^i	Me	Me	H
d;	$PhCH_2$	Me	Me	H
e;	Ph_2CH	Me	Me	H
f;	Me	Me	*p*-$ClC_6H_4CH_2$	H
g;	Et	Et	Me	Me
h;	$PhCH_2$	$PhCH_2$	Me	Ph
i;	-$[CH_2]_3$CHMe-		Me	
j;	Me		Me	Me
k;	Me		Me	Ph

Scheme.

isothiosemicarbazone gave (similarly) the corresponding *N*-vinyl-1,2,4-triazole (**6**; $R^1 = R^4 = H$), but in much lower yield than in the aromatic series. Our interest in cyclization with *N*-alkenylation led us to investigate the reaction of *N*(4)-(substituted vinyl)isothiosemicarbazones of unsymmetrical aliphatic ketones having different groups alpha to the (carbonyl) carbon in order to elucidate whether the introduction of unsaturation is non-selective or whether the orientation is controlled by some unknown factor(s). As was previously discussed for the aromatic series,[1] the reaction pathway of the *N*-alkenyltriazole formation involves Michael-type addition of N(1) to the ethylenic linkage of protonated esters (**4**) and *subsequent elimination* of ethyl cyano- or nitro-acetate (**9**) to leave a resonance-stabilized iminium cation. Abstraction of the more acidic alpha-hydrogen from the positively charged species, such as (**12**), should lead to the formation of an internal alkene,



(**12**)

whereas attack by a base on the less hindered hydrogen could afford a terminal alkene, *e.g.* (**6e**). In a preliminary experiment, it was found that the latter path was the one followed.

Thus the present work deals with an extension of *N*-alkenyl-1,2,4-triazole formation to aliphatic ketone 4-[2-cyano-2-(ethoxycarbonyl)vinyl]-3-alkylisothiosemicarbazones (**4**) and provides a novel route to *N*-alkenyl-1,2,4-triazoles with anti-Saytzeff orientation. The work also describes a direct cyclization–alkenylation reaction, 'cycloalkenylation,' of aliphatic ketone *N*(4)-unsubstituted isothiosemicarbazones (**1**) with ethyl β-ethoxy-α-nitroacrylate (**3**).

Results and Discussion

The cyclization of unsymmetrical ketone *N*(4)-(substituted vinyl)isothiosemicarbazones (**4b**—**e**) was performed by heating a solution of a compound (**4**) in acetic acid at 70 °C. The cleavage of compound (**4**) to an *N*-alkenyl-1,2,4-triazole (**6**) and (**9a**) was completed within 2 h. After removal of the acid and ethyl cyanoacetate (**9a**), the four samples of crude *N*-alkenyltriazole had the percentage compositions shown in the Table. 2-Methylcyclopentanone 3-methylisothiosemicarbazone (**1i**) did not give the corresponding compound (**4**) with enough purity for it to afford a reasonable analysis. This unsymmetrical cyclic ketone isothiosemicarbazone, however, gave the anti-Saytzeff product 1-(5-methylcyclopent-1-enyl)-3-methylthio-1*H*-1,2,4-triazole (**6i**) under the direct cycloalkenylation conditions in 71% yield, and no 2-methylcyclopent-1-enyl isomer was detected in the reaction mixture (Scheme).

From comparison of compound (**4b**) with (**4c**) or (**4d**) with (**4e**), the loss of proton from the iminium cation, as suggested before, should occur at the less crowded alpha-carbon, even though another pathway, in which an extended conjugation system was established, was available. Taking into account of the result of direct cycloalkenylation of isothiosemicarbazone (**1i**), we concluded that the introduction of unsaturation into *N*-alkenyl-1,2,4-triazoles is subject to strong steric but only weak electronic control. Thus bulkier bases may afford larger amounts of terminal alkene than do smaller ones. When propionic or benzoic acid was substituted for acetic acid, the percentage composition (**6b**)/(**6j**) of *N*-alkenyltriazoles from ester (**4b**) increased to 86/14 in these acids from 81/19 in acetic acid at the same temperature. The formation of the internal alkene (**6j**) was substantially inhibited [(**6b**)/(**6j**) ≥ 94/6] in pivalic acid where the reaction gave two major products, (**6b**) and (**8b**), in the molar ratio 1.0:0.8. This tendency for the formation of internal alkene (**6j**) to diminish when the acid was changed from acetic, through propionic or benzoic, to pivalic acid might be ascribed to the bulkiness of the base, probably a carboxylate ion that was liberated from the acid employed, rather than to the difference in acid strength. The competitive formation of the pivalate (**8b**) in pivalic acid may be a result of approach by the bulky base to the planar iminium carbon with comparable ease as that to the alpha-hydrogens. The percentage composition (**6b**)/(**6j**) was found to diminish to 71/29 in refluxing acetic acid. With increasing temperature the difference in reactivity at both alpha positions might become smaller, thereby resulting in the decreased selectivity. Unexpectedly, with stronger acids, *e.g.* formic or trichloroacetic acids, no conversion of ester (**4b**) into the corresponding products (**6**) and (**9**) occurred and the fused bicycle (**11b**) was the sole cyclized product. In formic acid, compound (**4d**) gave mainly the bicyclic ester (**10a**) which is often formed along with the triazole (**6**).

The yields* of triazoles (**6**) including those from symmetrical ketone *N*(4)-(substituted vinyl)isothiosemicarbazones (**4a**) and (**4f**—**h**) varied from 38—88% based on the amount of ester (**4**) that was initially used in the reaction and the overall yields calculated similarly from the amount of isothiosemicarbazone (**1**) amounted to 18—63%. If the isothiosemicarbazone (**1**) could be made to react with the cyanoacrylate (**2**) in acetic acid and the resulting intermediate (**4**) converted *in situ* into the corresponding triazole (**6**), there would be an improved yield of the last product. This process, however, was unsuccessful. Direct cycloalkenylation of compounds (**1**) could be realized on substitution of ethyl β-ethoxy-α-nitroacrylate (**3**) for the cyano analogue (**2**). Thus when *N*(4)-unsubstituted isothiosemicarbazones were heated with 6% excess of compound (**3**) in acetic acid, complete conversion of reactant (**1**) into product (**6**) occurred within 40 min and the yields of isolated triazoles (**6**) ranged from 38—78%. Further improvement in the yield of compounds (**6**) could be achieved by conducting the reaction in a mixture of acetic acid and acetonitrile. Under the latter conditions, cycloalkenylation was complete within 20 min and the yields of triazoles (**6**) increased to 66—82%. The reaction between isothiosemicarbazone (**1**) and nitroacrylate (**3**) should proceed through the initial condensation product (**5**) by analogy with the reaction of isothiosemicarbazone (**1**) with cyano analogue (**2**) . The compund (**5**) formed in the reaction mixture will rapidly be converted *in situ* into the corresponding alkenyltriazole (**6**) under the cycloalkenylation conditions. In some cases, 2(3)-(3-alkylthio-1,2,4-triazol-1-yl)alkan-2(3)-ylacetates (**7**) were obtained as minor products (13—29%); these compounds have never before been isolated from the cyclization mixture of compounds (**4**) and are considered to be characteristic of the cyclization of compounds (**4**; R^1 = aryl, and $R^2 = H$) derived from aromatic aldehydes.

The terminal methylene structure of compounds (**6a**—**f**) was supported in part by the appearance of a triplet (δ_C 101.56—107.79, $^1J_{CH}$ 161—163 Hz) in the vinylic region of the ^{13}C n.m.r. spectra. Further support was obtained from the ^1H n.m.r. spectra in which two vinylic protons† appeared at δ_H 4.57—4.90 and 5.33—5.86, each signal splitting into a multiplet due to long-range coupling. The internal alkenes (**6g**—**k**) were characterized by the vinylic carbon resonance near δ_C 115—122 as a doublet

* Throughout this text, the yields of *N*-alkenyl-1,2,4-triazoles refer to those for the purified products on chromatography.

† The upfield resonances for a given pair of vinylic protons could be assigned to the proton *trans* to the triazolyl group using the additivity principle of substituent shielding effects as previously described.[1]

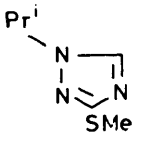
Table. Percentage compositions[a] of terminal and internal alkenes in the crude *N*-alkenyl-1,2,4-triazoles (**6**)

Starting compd.	Terminal/Internal
(**4b**)	81/19
(**4c**)	100/0
(**4d**)	60/40
(**4e**)	100/0

[a] Based on the peak area of the methylene- and the methyl-proton resonances of groups on the ethylenic carbons for terminal and internal alkenes, respectively.

($^1J_{CH}$ 155—156 Hz), with each component split into a multiplet, and were found to have the *E* configuration.* The ring carbon C-5 of triazoles (**6**) resonated within a narrow range of δ values, δ_C 141—142, as a doublet with large coupling constant ($^1J_{CH}$ 210—211 Hz).

Catalytic hydrogenation of compound (**6a**) over platinum gave the expected product, 1-isopropyl-3-methylthio-1*H*-1,2,4-triazole (**13**), structure of which was confirmed by comparison with an authentic compound obtained through the well known synthetic route.[4]



(**13**)

Triazolylmethyl acetates (**7**) were characterized by the strong i.r. carbonyl bands at 1 753—1 758 cm^{-1} and by the resonances of carbinol carbon, which appeared as a multiplet near δ_C 90—98; the resonance was shifted downfield as the number of carbon numbers in the R^1 and R^2 groups increased.

Experimental

Microanalyses were performed with a Perkin-Elmer 240D elemental analyser at the Microanalytical Laboratory of Kitasato University. I.r., u.v., and mass spectra were recorded on Perkin-Elmer 983, JASCO UVIDEC 610, and JMS-D-100 instruments, respectively. ^1H And ^{13}C n.m.r. spectra were obtained with a JNM-FX90Q spectrometer operating at 89.55 and 22.50 MHz, respectively. Preparative high-pressure liquid chromatography (h.p.l.c.) was carried out on a Kusano Kagaku KHLC-201 instrument with a 300 × 22 or a 300 × 15 mm glass column packed with silica gel.

(E,E)-4-*Unsubstituted Isothiosemicarbazones*.—*Isothiosemicarbazones* (**1b**—**i**) were obtained according to the literature method.[1] The oily compounds (**1d**), (**1e**), and (**1g**) were purified by column chromatography on silica gel with chloroform as eluant. The new compounds are as follows.

(**1b**) (86%), *pale yellow prisms*, m.p. 73—74.5 °C (from hexane) (Found: C, 45.3; H, 8.3; N, 26.7. $C_6H_{13}N_3S$ requires C, 45.25; H, 8.2; N, 26.4%).

(**1c**) (79%), *pale yellow prisms*, m.p. 61—63 °C (from hexane) (Found: C, 48.3; H, 8.7; N, 24.1. $C_7H_{15}N_3S$ requires C, 48.5; H, 8.7; N, 24.25%).

(**1d**) (78%), *pale yellow oil* (Found: C, 59.5; H, 6.75; N, 18.9. $C_{11}H_{15}N_3S$ requires C, 59.7; H, 6.8; N, 19.0%).

(**1e**) (82%), *pale yellow oil* (Found: C, 68.35; H, 6.4; N, 14.0. $C_{17}H_{19}N_3S$ requires C, 68.65; H, 6.4; N, 14.1%).

(**1f**) (20%), *needles*, m.p. 76.5—77.5 °C (from hexane) (Found: C, 51.55; H, 5.5; N, 16.6. $C_{11}H_{14}ClN_3S$ requires C, 51.7; H, 5.5; N, 16.4%).

(**1g**) (83%), *pale yellow oil* (Found: C, 48.7; H, 8.8; N, 24.5. $C_7H_{15}N_3S$ requires C, 48.5; H, 8.7; N, 24.25%).

(**1h**) (68%), *light yellow prisms*, m.p. 63—63.5 °C (from hexane) (Found: C, 68.75; H, 6.45; N, 14.0. $C_{17}H_{19}N_3S$ requires C, 68.65; H, 6.4; N, 14.1%).

(**1i**) (81%), *prisms*, m.p. 73—74 °C (from hexane) (Found: C, 52.05; H, 8.2; N, 23.0. $C_8H_{15}N_3S$ requires C, 51.9; H, 8.2; N, 22.7%).

Preparation of 4-(2-Cyano-2-ethoxycarbonylvinyl)-3-alkylisothiosemicarbazones.—Compounds (**4b**), (**4c**), (**4f**), and (**4g**) were obtained according to the literature procedure[5] and compounds (**4a**), (**4d**), (**4e**), and (**4h**) were prepared when an equimolar mixture of the required compound (**1**) and the ester (**2**) were kept in acetonitrile at room temperature for 1—3 days. New compounds are as follows.

(**4b**) (77%), *needles*, m.p. 104 °C (from Pr^iOH) (Found: C, 51.1; H, 6.5; N, 20.0. $C_{12}H_{18}N_4O_2S$ requires C, 51.05; H, 6.4; N, 19.8%); $\nu_{max.}(CCl_4)$ 3 198 (NH), 2 222 (CN), and 1 691 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.21 (3 H, t, *J* 7.3 Hz, =CCH$_2$*Me*), 1.34 (3 H, t, *J* 7.0 Hz, OCH$_2$*Me*), 2.06 (3 H, s, =CMe), 2.41 (2 H, q, *J* 7.3 Hz, =CC*H*$_2$Me), 2.53 (3 H, s, SMe), 4.29 (2 H, q, *J* 7.0 Hz, OC*H*$_2$Me), 7.66 (1 H, d, *J* 13.4 Hz, NHC*H*=), and 11.99 (1 H, d, *J* 13.4 Hz, N*H*CH=).

(**4c**) (48%), *needles*, m.p. 94—96 °C (from hexane) (Found: C, 52.4; H, 6.8; N, 18.7. $C_{13}H_{20}N_4O_2S$ requires C, 52.7; H, 6.8; N, 18.9%); $\nu_{max.}(CCl_4)$ 3 196 (NH), 2 222 (CN), and 1 693 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.20 (6 H, d, *J* 6.8 Hz, CH*Me*$_2$), 1.33 (3 H, t, *J* 7.0 Hz, CH$_2$*Me*), 2.04 (3 H, s, =CMe), 2.53 (3 H, s, SMe), 2.60 (1 H, quin, *J* 6.8 Hz, C*H*Me$_2$), 4.29 (2 H, q, *J* 7.0 Hz, C*H*$_2$Me), 7.65 (1 H, d, *J* 13.6 Hz, NHC*H*=), and 11.89 (1 H, d, *J* 13.6 Hz, N*H*CH=).

(**4d**) (62%), *light yellow crystalline powder*, m.p. 90—92 °C (from Pr^i_2O) (Found: C, 59.2; H, 5.9; N, 16.1. $C_{17}H_{20}N_4O_2S$ requires C, 59.3; H, 5.9; N, 16.3%); $\nu_{max.}(CCl_4)$ 3 192 (NH), 2 222 (CN), and 1 695 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.34 (3 H, t, *J* 7.0 Hz, CH$_2$*Me*), 2.01 (3 H, s, =CMe), 2.52 (3 H, s, SMe), 3.97 (2 H, s, C*H*$_2$Ph), 4.30 (2 H, q, *J* 7.0 Hz, C*H*$_2$Me), 7.26 (5 H, br s, Ph), 7.67 (1 H, d, *J* 13.4 Hz, NHC*H*=), and 12.08 (1 H, d, *J* 13.4 Hz, N*H*CH=).

(**4e**) (48%), *needles*, m.p. 127—129 °C (from Pr^i_2O) (Found: C, 65.6; H, 5.8; N, 13.1. $C_{23}H_{24}N_4O_2S$ requires C, 65.7; H, 5.75; N, 13.3%); $\nu_{max.}(CCl_4)$ 3 188 (NH), 2 222 (CN), and 1 693 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.34 (3 H, t, *J* 7.0 Hz, CH$_2$*Me*), 2.10 (3 H, s, =CMe), 2.52 (3 H, s, SMe), 4.28 (2 H, q, *J* 7.0 Hz, C*H*$_2$Me), 5.17 (1 H, s, C*H*Ph$_2$), 7.29 (10 H, s, Ph), 7.64 (1 H, d, *J* 13.4 Hz, NHC*H*=), and 11.82 (1 H, d, *J* 13.4 Hz, N*H*CH=).

(**4f**) (56%), *white fibre-like crystals*, m.p. 104—106 °C (from EtOH) (Found: C, 53.6; H, 5.4; N, 14.9. $C_{17}H_{19}ClN_4O_2S$ requires C, 53.9; H, 5.05; N, 14.8%); $\nu_{max.}(CCl_4)$ 3 196 (NH), 2 222 (CN), and 1 694 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.34 (3 H, t, *J* 7.0 Hz, CH$_2$*Me*), 2.07 and 2.13 (each 3 H, s, together Me$_2$C=), 4.28 (2 H, q, *J* 7.0 Hz, C*H*$_2$Me), 4.32 (2 H, s, SCH$_2$), 7.29 (4 H, s, *p*-ClC$_6$H$_4$), 7.63 (1 H, d, *J* 13.4 Hz, NHC*H*=), and 11.97 (1 H, d, *J* 13.4 Hz, N*H*CH=).

(**4g**) (32%), *light yellow needles*, m.p. 88—90 °C (from hexane) (Found: C, 52.7; H, 6.8; N, 19.2. $C_{13}H_{20}N_4O_2S$ requires C, 52.7; H, 6.8; N, 18.9%); $\nu_{max.}(CCl_4)$ 3 192 (NH), 2 222 (CN), and 1 694 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.08 and 1.22 (each 3 H, t, *J* 7.5 Hz, =CCH$_2$*Me*), 1.34 (3 H, t, *J* 7.0 Hz, OCH$_2$*Me*), 2.42 and 2.57 (each 2 H, q, *J* 7.5 Hz, =CC*H*$_2$Me), 2.53 (3 H, s, SMe), 4.29 (2 H, q, *J* 7.0 Hz, OC*H*$_2$Me), 7.66 (1 H, d, *J* 13.6 Hz, NHC*H*=), and 12.02 (1 H, d, *J* 13.6 Hz, N*H*CH=).

* The chemical-shift values (δ_H 5.85—7.44) of the vinylic proton were indicative of the hydrogen being *cis* to triazolyl.

(**4h**) (71%), *light yellow needles*, m.p. 122—124 °C (from Pr^i_2O) (Found: C, 65.7; H, 5.75; N, 13.3. $C_{23}H_{24}N_4O_2S$ requires C, 65.7; H, 5.75; N, 13.3%); $\nu_{max.}(CCl_4)$ 3 269 and 3 218 (NH), 2 225 (CN), and 1 679 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.36 (3 H, t, *J* 7.0 Hz, CH_2Me), 2.51 (3 H, s, SMe), 3.63 and 3.87 (each 2 H, s, CH_2Ph), 4.31 (2 H, q, *J* 7.0 Hz, CH_2Me), 7.25 (10 H, s, Ph), 7.69 (1 H, d, *J* 13.4 Hz, NHC*H*=), and 12.17 (1 H, d, *J* 13.4 Hz, N*H*CH=).

Preparation of 1-*Isopropenyl*-3-*methylthio*-1H-1,2,4-*triazole* (**6a**).—*General procedure for cyclization of compounds* (**4a—h**). A solution of compound (**4a**) (1.5 g, 5.6 mmol) in acetic acid (15 ml) was heated at 70 °C for 2 h and was then evaporated under reduced pressure. The residue was taken up in chloroform and the solution was thoroughly washed successively with 2% aqueous sodium hydroxide and with water to remove the residual acid and ethyl cyanoacetate. After being dried over anhydrous sodium sulphate, the organic solution was evaporated and the residual liquid (0.9 g) was subjected to column chromatography on silica gel (70 g) with chloroform as eluant. A homogeneous fraction gave the desired product (**6a**) as a *light yellow liquid* (0.57 g, 66%) (Found: C, 46.3; H, 5.9; N, 27.2. $C_6H_9N_3S$ requires C, 46.4; H, 5.8; N, 27.1%); $\lambda_{max.}$(EtOH) 206 and 260 nm (ε 18 300 and 18 900 $dm^3\ mol^{-1}\ cm^{-1}$); $\nu_{max.}(CCl_4)$ 1 658 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.26 (3 H, dd, $^4J_{HH}$ 1.3 and 0.7 Hz, =CMe), 2.61 (3 H, s, SMe), 4.81 and 5.51 (each 1 H, m, together $=CH_2$), and 8.19 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 102.61 (tq, $^1J_{CH}$ 163, $^3J_{CH}$ 5 Hz, $=CH_2$), 137.60 (m, =*C*Me), 141.39 (d, $^1J_{CH}$ 210 Hz, C-5 of triazole), and 162.57 (dq, $^3J_{CH}$ 4 and 13 Hz, C-3 of triazole); *m/z* 155 (M^+, 100%), 115 (30), 114 (23), and 41 (60).

General Procedure for Cyclization of Isothiosemicarbazones (**1a—h**) (*Direct Cycloalkenylation*).—A mixture of compound (**1a**) (0.29 g, 2 mmol), the nitroacrylate (**3**) 0.40 g, 2.12 mmol) (an *E*:*Z* 1:2 mixture, b.p. 161 °C/8—9 mmHg),[6] acetic acid (1 ml), and acetonitrile (4 ml) was heated at 70 °C for 20 min and was then evaporated at 40 °C (bath temperature) under reduced pressure. The residue was partitioned between 20% aqueous sodium carbonate and chloroform. The organic phase was washed successively with 2% aqueous sodium hydroxide and water, and was then dried over sodium sulphate. After evaporation of the solvent, the residual liquid (0.41 g) was subjected to preparative h.p.l.c. on silica gel, with a chloroform–dichloromethane mixture (1:1 v/v) as eluant, to give compound (**6a**) (0.23 g, 74.5%). The following new alkenyltriazoles were similarly prepared.*

(**6b**) (75/66%), *light yellow oil* (Found: C, 49.7; H, 6.6; N, 25.1. $C_7H_{11}N_3S$ requires C, 49.7; H, 6.55; N, 24.8%); $\lambda_{max.}$(EtOH) 204 and 259 nm (17 500 and 15 000); $\nu_{max.}(CCl_4)$ 1 650 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.20 (3 H, t, *J* 7 Hz, CH_2Me), 2.60 (2 H, q, *J* 7 Hz, CH_2Me), 2.61 (3 H, s, SMe), 4.86 and 5.46 (each 1 H, m, together $=CH_2$), and 8.21 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 101.56 (tt, $^1J_{CH}$ 162, $^3J_{CH}$ 5 Hz, $=CH_2$), 141.51 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), 143.93 (m, *C*=CH_2), and 162.35 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 169 (M^+, 100%), 115 (46), and 55 (21).

(**6c**) (57/74%), *light yellow oil* (Found: C, 52.6; H, 7.2; N, 23.1. $C_8H_{13}N_3S$ requires C, 52.4; H, 7.15; N, 22.9%); $\lambda_{max.}$(EtOH) 204 and 256 nm (19 000 and 13 300); $\nu_{max.}(CCl_4)$ 1 648 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.16 (6 H, d, *J* 6.8 Hz, $CHMe_2$), 2.61 (3 H, s, SMe), 3.02 (1 H, m, *J ca.* 7 Hz, $CHMe_2$), 4.90 and 5.33 (each 1 H, m, together $=CH_2$), and 8.18 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 102.05 (td, $^1J_{CH}$ 161, $^3J_{CH}$ 4 Hz, $=CH_2$), 142.19 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), 149.51 (m, *C*=CH_2), and 162.37 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 183 (M^+, 100%), 115 (40), 110 (49), and 41 (95).

(**6d**) (30/—%), *yellow oil* (Found: C, 62.5; H, 5.7; N, 18.25. $C_{12}H_{13}N_3S$ requires C, 62.3; H, 5.7; N, 18.2%); $\lambda_{max.}$(EtOH) 205 and 261 nm (39 600 and 18 600); $\nu_{max.}(CCl_4)$ 1 651 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.59 (3 H, s, SMe), 3.91 (2 H, s, CH_2Ph), 4.83 and 5.61 (each 1 H, m, together $=CH_2$), 7.26 (5 H, s, Ph), and 8.08 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 104.86 (tt, $^1J_{CH}$ 161, $^3J_{CH}$ 5 Hz, $=CH_2$), 141.98 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), and 162.50 (dq, $^3J_{CH}$ 4 and 13 Hz, C-3 of triazole); *m/z* 231 (M^+, 28%), 116 (100), and 115 (41).

(**6e**) (38/67%), *white prisms*, m.p. 106—108 °C (from Pr^i_2O) (Found: C, 70.2; H, 5.6; N, 13.6. $C_{18}H_{17}N_3S$ requires C, 70.3; H, 5.6; N, 13.7%); $\lambda_{max.}$(EtOH) 206 and 260 nm (30 000 and 17 200); $\nu_{max.}(CCl_4)$ 1 646 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.56 (3 H, s, SMe), 4.57 and 5.86 (each 1 H, m, together $=CH_2$), 5.47 (1 H, s, $CHPh_2$), 7.25 (10 H, m, Ph), and 8.03 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 107.79 (td, $^1J_{CH}$ 163, $^3J_{CH}$ 4 Hz, $=CH_2$), 142.26 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), 144.69 (m, *C*=CH_2), and 162.18 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 307 (M^+, 36%), 192 (100), and 115 (19).

(**6f**) (67/75%), *light yellow prisms*, m.p. 46—48 °C (from hexane) (Found: C, 54.15; H, 4.5; N, 15.7. $C_{12}H_{12}ClN_3S$ requires C, 54.2; H, 4.55; N, 15.8%); $\nu_{max.}(CCl_4)$ 1 658 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.24 (3 H, dd, $^4J_{HH}$ 1.3 and 0.6 Hz, =CMe), 4.32 (2 H, s, CH_2), 4.82 and 5.49 (each 1 H, m, together $=CH_2$), 7.24 and 7.36 (each 2 H, d, *J* 9 Hz, together *p*-ClC_6H_4), and 8.18 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 102.86 (tq, $^1J_{CH}$ 162, $^3J_{CH}$ 5 Hz, $=CH_2$), 137.80 (m, *C*=CH_2), 141.26 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), and 161.20 (dq, $^3J_{CH}$ 4 and 13 Hz, C-3 of triazole); *m/z* 265 (M^+, 47%), 232 (73), 127 (52), 125 (100), and 115 (19).

(**6g**) (61/82%), *light yellow oil* (Found: C, 52.6; H, 7.05; N, 23.2. $C_8H_{13}N_3S$ requires C, 52.4; H, 7.15; N, 22.9%); $\lambda_{max.}$(EtOH) 205 and 253 nm (13 300 and 9 400); $\nu_{max.}(CCl_4)$ 1 673 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.03 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.80 (3 H, d, *J* 7 Hz, =CH*Me*), 2.61 (3 H, s, SMe), 2.61 (2 H, q, *J* 7.5 Hz, CH_2Me), 5.85 (1 H, q, *J* 7 Hz, =C*H*Me), and 8.09 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 115.99 [d (each component split into a multiplet), $^1J_{CH}$ 155 Hz, =*C*HMe], 138.14 (m, *C*=CH), 142.00 (d, $^1J_{CH}$ 210 Hz, C-5 of triazole), and 161.91 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 183 (M^+, 22%), 136 (100), and 115 (11).

(**6h**) (88/77%), *needles*, m.p. 99—101 °C (from Pr^i_2O) (Found: C, 70.1; H, 5.5; N, 13.8. $C_{18}H_{17}N_3S$ requires C, 70.3; H, 5.6; N, 13.7%); $\nu_{max.}(CCl_4)$ 1 652 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.61 (3 H, s, SMe), 4.20 (2 H, s, CH_2Ph), 7.25 and 7.34 (each 5 H, s, Ph), 7.44 (1 H, s, =C*H*Ph), and 8.03 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 122.04 (d, $^1J_{CH}$ 156 Hz, =*C*HPh), 142.39 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), and 162.43 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 307 (M^+, 36%), 192 (100), 191 (46), and 115 (22).

(**6i**) (—/71%),† *oil* (Found: C, 55.1; H, 6.7; N, 21.4. $C_9H_{13}N_3S$ requires C, 55.4; H, 6.7; N, 21.5%); $\nu_{max.}(CCl_4)$ 1 657 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.17 (3 H, d, *J* 7 Hz, CH*Me*), 1.63—2.57 [4 H, m, $(CH_2)_2$], 2.62 (3 H, s, SMe), 3.24 (1 H, m, C*H*Me), 5.94 (1 H, m, C=CH), and 8.14 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 116.67 [d (each component split into a multiplet), $^1J_{CH}$ 168 Hz, C=*C*H], 141.76 (m, *C*=CH), 142.02 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), and 162.47 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 195 (M^+, 100%) and 148 (23).

(**6j**) [7%, obtained from a fraction following that of (**6b**)], *oil* (Found: C, 50.0; H, 6.5; N, 24.6. $C_7H_{11}N_3S$ requires C, 49.7; H, 6.55; N, 24.8%); $\lambda_{max.}$(EtOH) 205 and 256 nm (20 200 and 17 300); $\nu_{max.}(CCl_4)$ 1 678 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 1.79 (3 H, dq, $^3J_{HH}$ 7, $^5J_{HH}$ 1.2 Hz, =CH*Me*), 2.16 (3 H, quin, $^5J_{HH} = {}^4J_{HH}$ = 1.2 Hz, CH=C*Me*), 2.61 (3 H, s, SMe), 6.03 (1 H, qq, $^3J_{HH}$ 7, $^4J_{HH}$ 1.2 Hz, =C*H*Me), and 8.11 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$

* The yields (x) for cyclization of compounds (**4**) and those (y) for direct cycloalkenylation of isothiosemicarbazones (**1**) are given as (x/y%).

† Eluted with a dichloromethane–hexane (5:95 v/v) mixture.

115.23 [d (each component split into a multiplet), $^1J_{CH}$ 156 Hz, =*C*HMe], 131.87 (m, CH=*C*Me), 141.17 (d, $^1J_{CH}$ 210 Hz, C-5 of triazole), and 161.98 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 169 (M^+, 49%), 122 (100), and 115 (8).

(**6k**) [18%, obtained from a fraction following that of (**6d**)], *needles*, m.p. 60—61 °C (from Pr^i_2O) (Found: C, 62.5; H, 5.5; N, 18.3. $C_{12}H_{13}N_3S$ requires C, 62.3; H, 5.7; N, 18.2%); $\nu_{max.}(CCl_4)$ 1 661 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 2.40 (3 H, d, $^4J_{HH}$ 1.2 Hz, CH=C*Me*), 2.65 (3 H, s, SMe), 7.17 (1 H, q, $^4J_{HH}$ *ca.* 1 Hz, =C*H*Ph), 7.35 (5 H, s, Ph), and 8.27 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 119.31 (dq, $^1J_{CH}$ 160, $^3J_{CH}$ 7 Hz, =*C*HPh), 141.59 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), and 162.45 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 231 (M^+, 65%), 130 (23), 116 (100), and 115 (46).

Separation of 2-(3-*Methylthio*-1H-1,2,4-*triazol*-1-*yl*)*propan*-2-*yl Acetate* (**7a**).—After the fraction for compound (**6a**) had been separated under the cycloalkenylation conditions, elution was continued with chloroform–dichloromethane (1 : 1.5 v/v) to give compound (**7a**) (0.09 g, 21%) as prisms, m.p. 77—78 °C (from hexane) (Found: C, 44.6; H, 6.1; N, 19.45. $C_8H_{13}N_3O_2S$ requires C, 44.6; H, 6.1; N, 19.5%); $\nu_{max.}(CCl_4)$ 1 755vs cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.02 (3 H, s, COMe), 2.06 (6 H, s, CMe_2), 2.60 (3 H, s, SMe), and 8.33 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 90.24 (quin, $^2J_{CH}$ 4 Hz, *C*Me_2), 143.26 (d, $^1J_{CH}$ 212 Hz, C-5 of triazole), and 161.72 (dq, $^3J_{CH}$ 4 and 13 Hz, C-3 of triazole); *m/z* 215 (M^+, 15%), 157 (17), and 115 (100). The following new triazolylalkanyl acetates were obtained similarly.

(**7b**) (13%), *oil* (Found: C, 47.3; H, 6.7; N, 18.4. $C_9H_{15}N_3O_2S$ requires C, 47.15; H, 6.6; N, 18.3%); $\nu_{max.}(CCl_4)$ 1 755vs cm^{-1} (CO); $\delta_H(CDCl_3)$ 0.83 (3 H, t, *J* 8 Hz, CH_2*Me*), 2.06 (3 H, s, COMe), 2.40 (2 H, q, *J* 8 Hz, C*H*$_2$Me), 2.60 (3 H, s, SMe), and 8.30 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 93.56 [quin, $^2J_{CH}$ 5 Hz, *C*Me(Et)], 143.39 (d, $^1J_{CH}$ 212 Hz, C-5 of triazole), and 161.87 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 229 (M^+, 14%), 157 (18), and 115 (100).

(**7f**) (29%), *needles*, m.p. 70—71 °C (from hexane) (Found: C, 51.6; H, 5.0; N, 12.8. $C_{14}H_{16}ClN_3O_2S$ requires C, 51.6; H, 4.95; N, 12.9%); $\nu_{max.}(CCl_4)$ 1 753 vs cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.99 (3 H, s, COMe), 2.03 (6 H, s, CMe_2), 4.29 (2 H, s, CH_2), 7.25 and 7.31 (each 2 H, d, *J* 9 Hz, together *p*-ClC_6H_4), and 8.31 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 90.14 (quin, $^2J_{CH}$ 5 Hz, *C*Me_2), 143.26 (d, $^1J_{CH}$ 212 Hz, C-5 of triazole), and 160.18 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 325 (M^+, 4%), 267 (14), 225 (53), 125 (100), and 43 (67).

(**7g**) (19%), *oil* (Found: C, 49.2; H, 7.1; N, 17.2. $C_{10}H_{17}N_3O_2S$ requires C, 49.4; H, 7.0; N, 17.3%); $\nu_{max.}(CCl_4)$ 1 758 vs cm^{-1} (CO); $\delta_H(CDCl_3)$ 0.73 [6 H, t, *J* 7 Hz, $C(CH_2Me)_2$], 2.13 (3 H, s, COMe), 2.46 and 2.48 [each 2 H, q, *J* 7 Hz, together $C(CH_2Me)_2$], 2.59 (3 H, s, SMe), and 8.28 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 98.00 (m, *C*Et_2), 143.61 (d, $^1J_{CH}$ 213 Hz, C-5 of triazole), and 161.91 (dq, $^3J_{CH}$ 4 and 13 Hz, C-3 of triazole); *m/z* 243 (M^+, 15%), 157 (28), and 115 (100).

Cyclization of Ester (**4b**) *in Pivalic Acid: Formation of* 2-(3-*Methylthio*-1H-1,2,4-*triazol*-1-*yl*)*butan*-2-*yl Pivalate* (**8b**).—A mixture of compound (**4b**) (0.56 g, 2 mmol) and pivalic acid (3.0 g) was heated at 70 °C with agitation to afford a homogeneous solution, which was then heated at the same temperature for 6 h. The reaction mixture was neutralized with 10% aqueous sodium carbonate and extracted with chloroform. The extract was washed successively with 2% aqueous sodium hydroxide and then with water, dried over anhydrous sodium sulphate, and evaporated. The residual oil (0.42 g), consisting mainly of the triazoles (**6b**) and (**8b**) (1.0:0.8, molar ratio), was subjected to preparative h.p.l.c. (silica gel; dichloromethane) to give compound (**6b**) (0.12 g, 36%), and impure pivalate (**8b**) fraction [0.041 g, containing (**6j**) (6.9 mg)], and pure *pivalate* (**8b**) (0.086 g; the estimated total yield amounted to 22%), as an oil (Found: C, 53.1; H, 7.7; N, 15.7. $C_{12}H_{21}N_3O_2S$ requires C, 53.1; H, 7.8; N, 15.5%); $\nu_{max.}(CCl_4)$ 1 745 cm^{-1} (CO); $\delta_H(CDCl_3)$ 0.82 (3 H, t, *J* 7 Hz, CH_2*Me*), 1.20 (9 H, s, CMe_3), 2.03 (3 H, s, CMe), 2.40 (2 H, q, *J* 7 Hz, C*H*$_2$Me), 2.58 (3 H, s, SMe), and 8.26 (1 H, s, 5-H of triazole); $\delta_C(CDCl_3)$ 93.71 [m, *C*MeEt)], 143.07 (d, $^1J_{CH}$ 211 Hz, C-5 of triazole), and 161.72 (dq, $^3J_{CH}$ 5 and 13 Hz, C-3 of triazole); *m/z* 271 (M^+, 7%), 199 (24), 115 (43), and 57 (100).

Ethyl 2-*Methyl*-5-*methylthio*[1,2,4]*triazolo*[1,5-c]*pyrimidine*-8-*carboxylate* (**10a**).—This compound was obtained as a by-product from the reaction mixture of cyclization of either ester (**4b**) or (**4d**), in 1.6 and 3.5% yield, respectively. It was also prepared when ester (**4d**) (0.3 g, 0.9 mmol) was heated in formic acid (3 ml) at 70 °C for 1 h, and was obtained as *needles* (0.05 g, 23%), m.p. 121—122.5 °C (from Pr^iOH) (Found: C, 47.6; H, 4.75; N, 22.4. $C_{10}H_{12}N_4O_2S$ requires C, 47.6; H, 4.8; N, 22.2%); $\nu_{max.}(CCl_4)$ 1 715 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.45 (3 H, t, *J* 7 Hz, OCH_2*Me*), 2.70 (3 H, s, 2-Me), 2.79 (3 H, s, SMe), 4.51 (2 H, q, *J* 7 Hz, O*CH*$_2$Me), and 8.76 (1 H, s, 7-H); *m/z* 252 (M^+, 98%), 180 (100), and 107 (77).

Similarly, the *2-ethyl homologue* (**10b**) was obtained from a second fraction, after that of compound (**6g**), as light yellow needles (11%), m.p. 115—116.5 °C (from Pr^iOH) (Found: C, 49.8; H, 5.3; N, 20.9. $C_{11}H_{14}N_4O_2S$ requires C, 49.6; H, 5.3; N, 21.0%); $\nu_{max.}(CCl_4)$ 1 715 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.48 (6 H, t, *J* 7 Hz, 2-CH_2*Me* and OCH_2*Me*), 2.79 (3 H, s, SMe), 3.07 (2 H, q, *J* 7 Hz, 2-C*H*$_2$Me), 4.51 (2 H, q, *J* 7 Hz, O*CH*$_2$Me), and 8.73 (1 H, s, 7-H); *m/z* 266 (M^+, 75%), 220 (45), 194 (100), and 121 (60).

Preparation of Ethyl 2-*Ethyl*-2-*methyl*-5-*methylthio*-2,3-*dihydro*[1,2,4]*triazolo*[1,5-c]*pyrimidine*-8-*carboxylate* (**11b**).—A mixture of compound (**4b**) (0.15 g, 0.53 mmol) and trichloroacetic acid (1.5 g) was briefly warmed with agitation to obtain a clear solution, which was then heated at 70—75 °C for 2.5 h. The resulting yellow solution was made alkaline by addition of ice and sodium hydrogencarbonate, and was then extracted with chloroform. The extract was dried over anhydrous sodium sulphate and evaporated under reduced pressure to give substantially pure compound (**11b**) as yellow crystals (0.13 g, 87%), m.p. 112—113 °C (decomp.). Recrystallization from Pr^iOH gave *yellow needles*, m.p. 123.5 °C (decomp.) (Found: C, 51.1; H, 6.5; N, 20.0. $C_{12}H_{18}N_4O_2S$ requires C, 51.05; H, 6.4; N, 19.8%); $\nu_{max.}(CCl_4)$ 3 552 (NH) and 1 709 cm^{-1} (CO); $\delta_H(CDCl_3)$ 0.94 (3 H, t, *J* 7 Hz, 2-CH_2*Me*), 1.34 (3 H, t, *J* 7 Hz, OCH_2*Me*), 1.54 (3 H, s, 2-Me), 1.77 (2 H, q, *J* 7 Hz, 2-C*H*$_2$Me), 2.56 (3 H, s, SMe), 4.33 (2 H, q, *J* 7 Hz, O*CH*$_2$Me), 4.61 (1 H, s, NH), and 8.18 (1 H, s, 7-H); *m/z* 282 (M^+, 3%), 253 (100), and 108 (46).

This triazolopyrimidine (**11b**) was also obtained when a mixture of compound (**4b**) (0.5 g, 1.8 mmol), sodium acetate (1.0 g, 12 mmol), and ethanol (10 ml) was heated at 70 °C for 2 h, followed by evaporation of the reaction mixture, and extraction of the product with chloroform. Column chromatography (silica gel; chloroform) gave ester (**11b**) (0.1 g, 20%).

Hydrogenation of Compound (**6a**). *Preparation of* 1-*Isopropyl*-3-*methylthio*-1H-1,2,4-*triazole* (**13**).—A mixture of the isopropenyltriazole (**6a**) (0.39 g), platinum(IV) oxide (0.08 g), and methanol (4 ml) was stirred under hydrogen at room temperature and atmospheric pressure for 24 h. The catalyst was filtered off with the aid of active charcoal and the filtrate was evaporated. Column chromatography of the residue (0.35 g) on silica gel with chloroform as eluant gave the reduced product (**13**) as a liquid (0.17 g, 43%) (Found: C, 45.8; H, 6.9; N, 26.7. Calc. for $C_6H_{11}N_3S$: C, 45.8; H, 7.05; N, 26.7%); $\delta_H(CDCl_3)$ 1.53 (6 H, d, *J* 7 Hz, Me_2CH), 2.58 (3 H, s, SMe), 4.48 (1 H, hept, *J* 7 Hz, Me_2CH), and 8.01 (1 H, s, 5-H); *m/z* 157 (M^+,

34%), 115 (77), and 43 (100). This product was identical with an authentic compound prepared according to the known process[4] which consists of *S*-methylation of 1-isopropylthiosemicarbazide[7] and cyclization of the thus obtained isothiosemicarbazide with hot formic acid.

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