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PALLADIUM-CATALYZED POLYHETERO-CLAISEN REARRANGEMENT OF 4-ALLYLTHIOPYRIMIDIN-2(1H)-ONES AND 5-ALLYLTHIO-1,2,4-TRIAZIN-3(2H)-ONES

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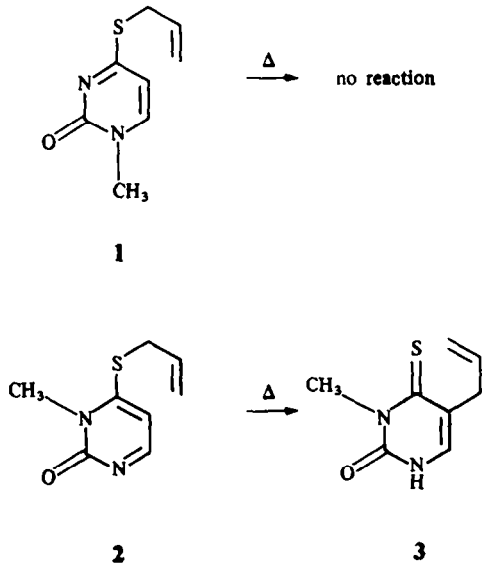
Abstract—The S → N allylic transposition of 4-allylthiopyrimidin-2(1H)-ones **4** and 5-allylthio-1,2,4-triazin-3(2H)-ones **5** has been performed successfully by catalysis of palladium(II) salts. In both cases the N-alkylated products (**6** and **7**) are obtained with no traces of the C-alkylated products.

Aromatic thio-Claisen rearrangement has been studied extensively owing to its synthetic utility.[1] The nitrogen containing heteroaromatic thio-Claisen rearrangement (the S → C rearrangement) is well known,[1] however, examples of the S → N rearrangements are very scarce. The S → N allylic rearrangements of 2-allylthioimidazoles[2] and 2-allylthiobenzthiazoles[3] are typical examples. It has been reported that 5-allylthiopyrimidines,[4] 8-allylthiocaffeines,[2] 3-allylthio-1,2,4-triazin-5(2H)-ones[5] and 2-allylthiopyrimidin-4(3H)-ones[6] do not rearrange, or provide the expected rearranged products in low yields.

Recently we have demonstrated that a Pd-salt very effectively catalyzes the rearrangement of the latter two examples.[5,6] We also found that a similar catalytic system effected the S → N allylic transposition of 4-allylthiopyrimidin-2(1H)-ones **4** and 5-allylthio-1,2,4-triazin-3(2H)-ones **5**. In this paper we describe the results of the systematic investigation on this novel rearrangement.

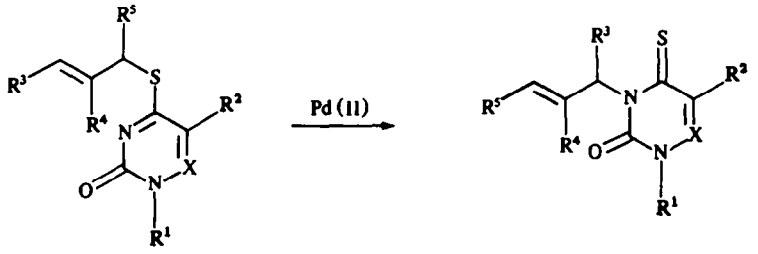


Scheme 1.

RESULTS AND DISCUSSION

Fourrey *et al.*[7] have noted that 4-allylthiopyrimidin-2-ones: 4-allylthiopyrimidin-2(3H)-one **2** undergoes the S → C rearrangement very smoothly, however the thermal rearrangement of the corresponding (1H)-one analogue **1** is not induced (Scheme 1). After confirmation of these results, we applied our Pd catalyst system to **1** and found that the S → N allylic transposition of **1** proceeded very smoothly in the presence of 2 mol% of bis(benzonitrile)-palladium(II) chloride by refluxing for 2 hr in tetrahydrofuran (THF) under an N_2 atmosphere. 1-Methyl-3-allyl-4-thiouracil (**6h**) was isolated in quantitative yield (**1** = **4h**, entry 8, Table 1).

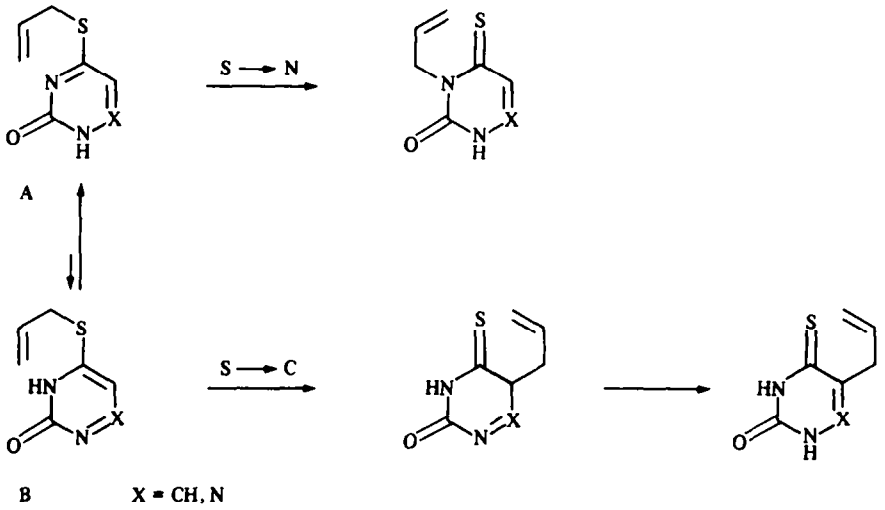
Encouraged by this result, we next examined the rearrangement of 4-allylthiopyrimidin-2(1H)-ones bearing no substituent on the N-1 position (R^1 = H, Scheme 2), by systematically changing the substituents R^2–R^6. By the catalysis of 2 mol% of Pd(II) salt, **4a** underwent the specific S → N rearrangement and yielded **6a** as a single product (entry 1). The S → C(5) rearranged product was not detected by thorough examination of the reaction mixture by means of TLC and ^{1}H-NMR. The structure of **6a** was determined by its ^{1}H-NMR spectrum, which shows the presence of the olefinic proton on C-5 carbon. In the absence of the Pd(II) salt, **4a** was stable under xylene reflux. At 150° (neat), **4a** decomposed to give an intractable mixture of products. The specific N-3 allylation may be primarily ascribed to the predominance of the tautomer A in the equilibrium with the tautomer B (Scheme 3).[8] A similar specific or preferential S → N rearrangement over the S → C rearrangement was reported for the Pd(II)-catalyzed rearrangement of S-allylthioimidates.[9] The specificity of the S → N allylic transposition is generally seen from the results summarized in Table 1 (entries 1–7). The reaction proceeded very smoothly, independent of the electronic nature of the substituent R^2 (entries 1–



4 X = C—R⁶
5 X = N

6 X = C—R⁶
7 X = N

Scheme 2.



A

B X = CH, N

Scheme 3.

4). No significant differences of reactivity were discernible among the cases of $R^2 = H$, $R^2 = CH_3$ and $R^2 = F$. However, the reactivity is highly dependent on the substitution pattern of the allylic moiety. In the case of $R^5 = CH_3$ (entry 7), the reaction proceeded smoothly and provided the N-3-crotyl product **6g** in quantitative yield. When $R^3 = CH_3$, no rearrangement took place even in refluxing dioxane. This may be due to a repulsive pseudo-A(1,3) interaction[10] between C-2 (pyrimidine) carbonyl oxygen and the terminal R^3

Table 1. Palladium-catalyzed S → N allylic rearrangement of 4-allylthiopyrimidin-2(1H)-ones (**4**) and 5-allylthio-1,2,4-triazin-3(2H)-ones (**5**)

Entry	4 or 5	Substrate						Pd[a] (mol%)	Reaction conditions[b]	Conversion (%)	Product 6 or 7	Yield[c] (%)
		R^1	R^2	R^3	R^4	R^5	R^6					
1	**4a**	H	H	H	H	H	H	2	THF, 3 hr	93	**6a**	90
2	**4b**	H	CH_3	H	H	H	H	2	THF, 2 hr	100	**6b**	93
3	**4c**	H	F	H	H	H	H	2	THF, 2 hr	100	**6c**	92
4	**4d**	H	H	H	H	H	CH_3	2	THF, 2 hr	100	**6d**	96
5	**4e**	H	H	CH_3	H	H	H	10	Dioxane, 10 hr	0	—	—
6	**4f**	H	H	H	CH_3	H	H	10	Dioxane, 11 hr	51	**6f**	38
7[d]	**4g**	H	CH_3	H	H	CH_3	H	2	THF, 2 hr	100	**6g**	100
8	**4h**	CH_3	H	H	H	H	H	2	THF, 2 hr	100	**6h**	100
9	**5a**	H	H	H	H	H	—	1	THF, 1 hr	100	**7a**	97
10	**5b**	H	CH_3	H	H	H	—	1	THF, 1 hr	100	**7b**	82
11	**5e**	H	H	CH_3	H	H	—	5	THF, 5 hr	65	**7e**	77

[a] $PdCl_2(PhCN)_2$ as a catalyst.
[b] At the reflux temp.
[c] Isolated yields based on conversions.
[d] A mixture with 4-crotylthio-5-methylpyrimidin-2(1H)-one (**4e**) (**4g**:**4e** = 57:43), see Experimental.

methyl group in a six-membered chairlike transition state. The rearrangement of **4f** was very slow, resulting in low yield.

5-Allylthio-1,2,4-triazin-3(2H)-ones **5** showed a similar reactivity to **4**. The starting material **5a** was recovered completely under xylene reflux. Heating at 150° for 2 hr of **5a** (neat) provided 4-allyl-5-thio-1,2,4-triazine-3,5(2H,4H)-dione **7a** in 38% yield based on 79% conversion. In contrast in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ the rearrangement of **5a** proceeded very smoothly at the refluxing temperature of THF and **7a** was obtained almost quantitatively (entry 9). The specific S → N rearrangement also resulted with other triazines (entries 10 and 11).

In entry 11, only the methallyl-type product was obtained with no trace of the crotyl-type product while in entry 7, only the crotyl-type product was afforded without the formation of the methallyl-type product. These complete allylic inversions indicate that the reaction proceeded in an intramolecular fashion.

All these results are explained in the same manner as in the case of the Pd(II)-catalyzed S → N allylic transposition of S-allylthioimidates reported previously and support the mechanism proposed therein.[11]

Generally alkylation at the N-3 (pyrimidine) or at the N-4 (triazine) position is known to proceed in undesirable yields.[4,12] The efficiency of the present method is apparent from the high structural flexibility and ready availability of the starting material as well as its high yield with a lack of side products.

EXPERIMENTAL

M.ps were determined in capillary tubes with a Mettler FP 61 instrument and uncorrected. Short-path (bulb-to-bulb) distillation was carried out in a Kugelrohr apparatus. Microanalyses were obtained with a Perkin–Elmer 240 or 240B instrument. Measurement of IR spectra was made on a Hitachi 260-10 spectrometer. ^{1}H-NMR were measured at 60 MHz on a Hitachi R-24B NMR spectrometer using tetramethylsilane as an internal standard. Mass spectra were run on a Shimadzu LKB-9000B instrument.

General procedure for preparation of 4-allylthiopyrimidin-2(1H)-ones (**4a–g**) *and 5-allylthio-1,2,4-triazin-3(2H)-ones* (**5**)

To a stirred soln of 4-thiouracil ($R^1 = R^2 = R^6 = H$ (**4a, 4e, 4f**), $R^1 = R^6 = H$, $R^2 = CH_3$ (**4b, 4g**), $R^1 = R^6 = H$, $R^2 = F$ (**4c**), $R^1 = R^2 = H$, $R^6 = CH_3$ (**4d**); 10 mmol) or 4-thio-6-azauracil ($R^1 = R^2 = H$ (**5a, 5e**), $R^1 = H$, $R^2 = CH_3$ (**5b**); 10 mmol) and sodium methoxide (11 mmol) in MeOH (30 ml) was added allyl halide (allyl bromide (**4a–d, 5a,b**), *trans*-crotyl bromide (**4e, 5e**), methallyl chloride (**4f**), 3-chloro-1-butene (**4g**); 13 mmol) at room temp. The mixture was stirred overnight at the same temp. After removal of the solvent under reduced pressure, the residue was partitioned between $CHCl_3$ and H_2O, and then the organic extract was dried over $MgSO_4$. Evaporation of the solvent gave crude **4** or **5**, which was recrystallized from EtOH (**4a**), n-hexane–EtOH (**4b–f**) or n-hexane–acetone (**5**). In the case of the preparation of **4g**, a similar extractive workup provided a yellow solid, which was recrystallized from n-hexane–acetone to give a mixture of **4g** and **4e** (combined yield 17.3%; **4g**:**4e** = 57:43 from ^{1}H-NMR analysis).

4-*Allylthiopyrimidin*-2(1H)-*one* (**4a**)

Yield 79.8%; m.p. 157.7°; IR (Nujol, cm^{-1}) 1630s, 1405m, 1240m, 1190m, 915m; ^{1}H-NMR ($CDCl_3$) δ 3.86 (d, J = 6.0 Hz, 2H), 4.98–5.43 (m, 2H), 5.59–6.20 (m, 1H), 6.23 (d, J = 6.6 Hz, 1H), 7.45 (d, J = 6.6 Hz, 1H); mass *m/e* (relative intensity) 168 (M^+, 7), 167 (5), 153 (100), 68 (16), 41 (24), 39 (24). (Calc for $C_5H_6N_2OS$: C, 49.98; H, 4.79; N, 16.66; S, 19.06. Found: C, 49.78; H, 4.76; N, 16.71; S, 19.03%.)

4-*Allylthio*-5-*methylpyrimidin*-2(1H)-*one* (**4b**)

Yield 70.3%; m.p. 170.5°; IR (Nujol, cm^{-1}) 1640s, 1610s, 1360m, 1070m, 910m, 775m; ^{1}H-NMR ($CDCl_3$) δ 2.00 (s, 3H), 3.85 (d, J = 6.6 Hz, 2H), 4.97–6.23 (m, 3H), 7.23 (s, 1H); mass *m/e* (relative intensity) 182 (M^+, 17), 167 (100), 149 (17), 71 (15), 41 (20), 39 (35). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.79; H, 5.67; N, 15.27; S, 17.43%.)

4-*Allylthio*-5-*fluoropyrimidin*-2(1H)-*one* (**4c**)

Yield 52.8%; m.p. 150.0°; IR (Nujol, cm^{-1}) 1650s, 1630s, 1380m, 1315m, 1075m, 910m, 790m; ^{1}H-NMR ($CDCl_3$) δ 3.86 (d, J = 5.4 Hz, 2H), 5.03–6.14 (m, 3H), 7.40 (d, J = 3.0 Hz, 1H); mass *m/e* (relative intensity) 186 (M^+, 17), 171 (100), 153 (14), 74 (11), 41 (33), 39 (33). (Calc for $C_7H_7N_2OSF$: C, 45.15; H, 3.79; N, 15.05; S, 17.22. Found: C, 45.18; H, 3.87; N, 15.07; S, 17.34%.)

4-*Allylthio*-6-*methylpyrimidin*-2(1H)-*one* (**4d**)

Yield 32.0%; m.p. 152.5°; IR (Nujol, cm^{-1}) 1660s, 1600s, 1265m, 1095m, 920m; ^{1}H-NMR ($CDCl_3$) δ 2.37 (s, 3H), 3.96 (d, J = 6.6 Hz, 2H), 5.05–5.48 (m, 2H), 5.66–6.20 (m, 1H), 6.13 (s, 1H); mass *m/e* (relative intensity) 182 (M^+, 12), 167 (100), 141 (19), 82 (16), 39 (24). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.54; H, 5.64; N, 15.44; S, 17.62%.)

4-Trans-*crotylthiopyrimidin*-2(1H)-*one* (**4e**)

Yield 80.2%; m.p. 139.3°; IR (Nujol, cm^{-1}) 1640s, 1610s, 1405m, 1240m, 1090m; ^{1}H-NMR ($CDCl_3$) δ 1.67 (d, J = 4.8 Hz, 3H), 3.78 (d, J = 5.4 Hz, 2H), 5.21–5.93 (m, 2H), 6.06 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H); mass *m/e* (relative intensity) 182 (M^+, 26), 167 (100), 153 (24), 149 (50), 128 (31), 86 (22), 55 (61), 39 (24). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.57; H, 5.56; N, 15.63; S, 17.57%.)

4-*Methallylthiopyrimidin*-2(1H)-*one* (**4f**)

Yield 40.6%; m.p. 133.0°; IR (Nujol, cm^{-1}) 1630s, 1605s, 1400m, 1240m, 1085m; ^{1}H-NMR ($CDCl_3$) δ 1.83 (s, 3H), 3.88 (s, 2H), 4.86 (br s, 1H), 5.00 (br s, 1H), 6.19 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H); mass *m/e* (relative intensity) 182 (M^+, 7), 167 (100), 149 (21), 68 (11), 39 (16). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.63; H, 5.57; N, 15.57; S, 17.58%.)

4-(1-*Methyl*-2-*propenyl*)*thio*-5-*methylpyrimidin*-2(1H)-*one* (**4g**)

^{1}H-NMR ($CDCl_3$) δ 1.55 (d, J = 6.6 Hz, 3H), 2.02 (s, 3H), 4.6–6.2 (m, 4H), 7.30 (s, 1H).

5-*Allylthio*-1,2,4-*triazin*-3(2H)-*one* (**5a**)

Yield 73.6%; m.p. 74.4°; IR (Nujol, cm^{-1}) 1670m, 1620m, 1560s, 1250m, 1080m; ^{1}H-NMR ($CDCl_3$) δ 3.84 (d, J = 6.0 Hz, 2H), 5.00–5.45 (m, 2H), 5.53–6.22 (m, 1H), 7.51 (s, 1H); mass *m/e* (relative intensity) 169 (M^+, 1), 154 (100), 128 (39), 72 (21), 41 (40), 39 (30). (Calc for $C_6H_7N_3OS$: C, 42.59; H, 4.17; N, 24.83; S, 18.95. Found: C, 42.69; H, 4.19; N, 24.68; S, 19.11%.)

5-*Allylthio*-6-*methyl*-1,2,4-*triazin*-3(2H)-*one* (**5b**)

Yield 52.5%; m.p. 143.0°; IR (Nujol, cm^{-1}) 3200w, 3060w, 1650s, 1585s, 1320m, 1070s, 955m; ^{1}H-NMR ($CDCl_3$) δ 2.29 (s, 3H), 3.92 (d, J = 6.0 Hz, 2H), 5.10–6.19 (m, 3H); mass *m/e* (relative intensity) 183 (M^+, 13), 168 (100), 142 (29), 86 (22), 41 (29). (Calc for $C_7H_9N_3OS$: C, 45.89; H, 4.95; N, 22.94; S, 17.50. Found: C, 46.05; H, 5.08; N, 22.83; S, 17.28%.)

5-Trans-*crotylthio*-1,2,4-*triazin*-3(2H)-*one* (**5e**)

Yield 14.2%; m.p. 114.4°; IR (Nujol, cm^{-1}) 3120w, 3020w, 1670m, 1605s, 1555s, 1240m, 1180m; ^{1}H-NMR ($CDCl_3$) δ 1.68

(d, J = 5.4 Hz, 3H), 3.83 (d, J = 5.4 Hz, 2H), 5.27–6.15 (m, 4H), 7.66 (s, 1H); mass *m/e* (relative intensity) 183 (M^+, 2), 168 (100), 128 (32), 72 (20), 55 (71). (Calc for $C_7H_9N_3OS$: C, 45.89; H, 4.95; N, 22.94; S, 17.50. Found: C, 45.82; H, 4.93; N, 22.88; S, 17.47%.)

1-*Methyl*-4-*allylthiopyrimidin*-2(1H)-*one* (**4h**)

Into a suspension of NaH (63% assay, 168 mg, 4.4 mmol) in DMF (15 ml) was added **4a** (673 mg, 4 mmol) at room temp. After stirring at the same temp for 30 min under N_2, MeI (375 μl, 6 mmol) was added, and then the mixture was stirred for 1 hr. Usual extractive workup with $CHCl_3$ gave crude **4h**, which was subjected to column chromatography (silica gel, n-hexane–acetone gradient) to provide pure **4h** (404 mg, 55.4% yield). The analytically pure compound was obtained by recrystallization from n-hexane–acetone: m.p. 122.7°; IR (Nujol, cm^{-1}) 1645s, 1600m, 1490m, 1320m, 1050m, 950m; ^{1}H-NMR ($CDCl_3$) δ 3.42 (s, 3H), 3.83 (d, J = 6.6 Hz, 2H), 4.93–5.37 (m, 2H), 5.54–5.92 (m, 1H), 6.07 (d, J = 6.6 Hz, 1H), 7.24 (d, J = 6.6 Hz, 1H); mass *m/e* (relative intensity) 182 (M^+, 7), 167 (100), 141 (22), 100 (8), 42 (21). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.85; H, 5.55; N, 15.42; S, 17.30%.)

S → N *Allylic rearrangement*

(*a*) *Thermal rearrangement*

Treatment of **4a** in refluxing xylene for 7 hr under N_2 provided only the starting material. The complete recovery and the absence of **6a** were thoroughly checked by TLC and ^{1}H-NMR.

Under N_2 **5a** was heated (neat, 169 mg, 1 mmol) at 150° for 2 hr. After cooling, the mixture was directly subjected to column chromatography (silica gel, n-hexane–acetone gradient) to give **7a** (51 mg) and the starting material **5a** (35 mg). The yield of the rearranged products was 38% on the basis of 79% conversion.

(*b*) Pd(II)-*Catalyzed* S → N *allylic rearrangement*

General procedure. A THF or dioxane soln of **4** or **5** (in the case of entry 7 in Table 1, a mixture of **4g** and **4e** (57 : 43) was used; 1 mmol) and $PdCl_2(PhCN)_2$ amounts and conditions are shown in Table 1. After evaporation of the solvent, the residue was directly subjected to a column purification (silica gel, n-hexane–acetone gradient) to give the spectroscopically pure compound **6** or **7**. Analytically pure samples were obtained by recrystallization from n-hexane–acetone or by distillation.

3-*Allyl*-4-*thiouracil* (**6a**)

M.p. 157.9°; IR (Nujol, cm^{-1}) 3200w, 3060w, 1680s, 1600s, 1420m, 1190m, 1110m, 795m; ^{1}H-NMR ($CDCl_3$–acetone-d_6) δ 4.92–5.37 (m, 4H), 5.59–6.21 (m, 1H), 6.44 (d, J = 7.2 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H); mass *m/e* (relative intensity) 168 (M^+, 20), 153 (100), 86 (10), 39 (14). (Calc for $C_7H_8N_2OS$: C, 49.98; H, 4.79; N, 16.66; S, 19.06. Found: C, 50.10; H, 4.84; N, 16.57; S, 19.15%.)

3-*Allyl*-5-*methyl*-4-*thiouracil* (**6b**)

M.p. 115.8°; IR (Nujol, cm^{-1}) 3180w, 3050w, 1685s, 1615s, 1415m, 1340m, 1190m, 1115m, 1020m; ^{1}H-NMR ($CDCl_3$) δ 2.10 (s, 3H), 4.98–5.36 (m, 4H), 5.57–6.18 (m, 1H), 7.02 (d, J = 5.4 Hz, 1H); mass *m/e* (relative intensity) 182 (M^+, 27), 167 (100), 71 (11), 39 (19). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.71; H, 5.58; N, 15.31; S, 17.75%.)

3-*Allyl*-5-*fluoro*-4-*thiouracil* (**6c**)

M.p. 136.5°; IR (Nujol, cm^{-1}) 3140w, 3050w, 1670s, 1630s, 1430m, 1250m, 1200m, 770m; ^{1}H-NMR ($CDCl_3$) δ 4.93–5.40 (m, 4H), 5.54–6.18 (m, 1H), 7.08 (d, J = 1.8 Hz, 1H); mass *m/e* (relative intensity) 186 (M^+, 97), 171 (100), 104 (9), 41 (14), 39 (21). (Calc for $C_7H_7N_2OSF$: C, 45.15; H, 3.79; N, 15.05; S, 17.22. Found: C, 45.20; H, 3.83; N, 14.94; S, 17.22%.)

3-*Allyl*-6-*methyl*-4-*thiouracil* (**6d**)

M.p. 172.4°; IR (Nujol, cm^{-1}) 3200w, 3060w, 1685s, 1620s, 1325m, 1240s, 1095m; ^{1}H-NMR ($CDCl_3$) δ 2.07 (s, 3H), 4.94–5.37 (m, 4H), 5.55–6.20 (m, 1H), 6.43 (s, 1H); mass *m/e* (relative intensity) 182 (M^+, 28), 167 (100), 100 (9), 41 (12), 39 (12). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.93; H, 5.58; N, 15.33; S, 17.38%.)

3-*Methallyl*-4-*thiouracil* (**6f**)

M.p. 113.7°; IR (Nujol, cm^{-1}) 3210w, 3080m, 1690s, 1610s, 1420m, 1180s, 1150m; ^{1}H-NMR ($CDCl_3$) δ 1.80 (s, 3H), 4.53 (br s, 1H), 4.78 (br s, 1H), 4.92 (s, 2H), 6.44 (d, J = 7.2 Hz, 1H), 6.86 (dd, J = 6.0, 7.2 Hz, 1H); mass *m/e* (relative intensity) 182 (M^+, 21), 167 (100), 86 (9), 39 (12). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.71; H, 5.57; N, 15.32; S, 17.59%.)

4-*Crotyl*-5-*methyl*-4-*thiouracil* (**6g**)

M.p. 150.7°; IR (Nujol, cm^{-1}) 3220w, 3150w, 1700s, 1640s, 1355m, 1230m, 1190m, 1110m, 770m; ^{1}H-NMR ($CDCl_3$) δ 1.66 (d, J = 4.8 Hz, 3H), 2.10 (s, 3H), 5.03 (d, J = 4.8 Hz, 2H), 5.17–6.06 (m, 2H), 7.02 (d, J = 5.4 Hz, 1H); mass *m/e* (relative intensity) 196 (M^+, 30), 167 (100), 142 (11), 81 (9), 55 (9). (Calc for $C_9H_{12}N_2OS$: C, 55.06; H, 6.16; N, 14.27; S, 16.34. Found: C, 55.10; H, 6.27; N, 14.25; S, 16.06%.)

1-*Methyl*-3-*allyl*-4-*thiouracil* (**6h**)

B.p. 153–158° (0.75 mm Hg); IR (neat, cm^{-1}) 3080w, 2930w, 1680s, 1610s, 1370m, 1330m, 1205s, 1115m, 765m; ^{1}H-NMR ($CDCl_3$) δ 3.40 (s, 3H), 5.00–5.43 (m, 4H), 5.63–6.27 (m, 1H), 6.51 (d, J = 7.8 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H); mass *m/e* (relative intensity) 182 (M^+, 28), 167 (100), 98 (5), 42 (17). (Calc for $C_8H_{10}N_2OS$: C, 52.73; H, 5.53; N, 15.38; S, 17.60. Found: C, 52.56; H, 5.64; N, 15.77; S, 17.71%.)

4-*Allyl*-5-*thio*-1,2,4-*triazine*-3,5(2H,4H)-*dione* (**7a**)

M.p. 84.9°; IR (Nujol, cm^{-1}) 3270m, 3070w, 1670s, 1570m, 1410m, 1300m, 1185s, 1080m, 730m; ^{1}H-NMR ($CDCl_3$) δ 4.36 (d, J = 5.4 Hz, 2H), 5.03–5.40 (m, 2H), 5.50–6.12 (m, 1H), 7.61 (s, 1H); mass *m/e* (relative intensity) 169 (M^+, 20), 154 (100), 72 (16), 41 (24), 39 (24). (Calc for $C_6H_7N_3OS$: C, 42.59; H, 4.17; N, 24.83; S, 18.95. Found: C, 43.35; H, 4.17; N, 25.28; S, 18.57%.)

4-*Allyl*-5-*thio*-6-*methyl*-1,2,4-*triazine*-3,5(2H,4H)-*dione* (**7b**)

M.p. 100.9°; IR (Nujol, cm^{-1}) 1680s, 1575m, 1320s, 1210s, 1115m; ^{1}H-NMR ($CDCl_3$) δ 2.43 (s, 3H), 5.00–5.41 (m, 4H), 5.65–6.17 (m, 1H); mass *m/e* (relative intensity) 183 (M^+, 21), 168 (100), 142 (9), 72 (11), 41 (22). (Calc for $C_7H_9N_3OS$: C, 45.89; H, 4.95; N, 22.94; S, 17.50. Found: C, 45.79; H, 4.99; N, 22.96; S, 17.37%.)

4-*Methallyl*-5-*thio*-1,2,4-*triazine*-3,5(2H,4H)-*dione* (**7e**)

B.p. 142–145° (0.6 mm Hg); IR (neat, cm^{-1}) 3180–3400 br m, 2900w, 1695s, 1575m, 1360m, 1245s; ^{1}H-NMR ($CDCl_3$) δ 1.64 (d, J = 6.6 Hz, 3H), 5.10–5.50 (m, 2H), 5.99–6.47 (m, 2H), 7.79 (s, 1H); mass *m/e* (relative intensity) 183 (M^+, 21), 168 (100), 130 (9), 112 (11), 55 (24). (Calc for $C_7H_9N_3OS$: C, 45.89; H, 4.95; N, 22.94; S, 17.50. Found: C, 46.05; H, 5.13; N, 22.68; S, 17.43%.)

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