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THIO-CLAISEN REARRANGEMENTS OF SOME KETENE DERIVATIVES

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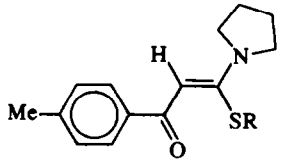
Abstract—A number of 1-allylthio and 1-crotylthio 1-aminoalkenes derived from ketones and active methylene compounds has been prepared and rearranged to the corresponding thioamides (thio-Claisen rearrangement). Besides rearrangement products, small amounts of 1-alkyl-thio-N-alkyl-N-phenyl-1-aminoalkenes have also been isolated. When the ketene derivatives did possess a H-atom on nitrogen, cleavage of the formed thioamide produced phenyl isothiocyanate and substituted active methylene compounds.

INTRODUCTION

Rearrangements of S-alkylated thioamides and of ketene-N,O-acetals are known.[1-3] In continuation of our work on thio-Claisen rearrangements on ketene-S,S-acetals derived from ketones[4] and from active methylene compounds,[5-7] we have now investigated the rearrangement of the corresponding 1 - alkylthio - 1 - aminoalkenes. The influence of an arylamino group as compared with an alkylthio group was also of potential interest.



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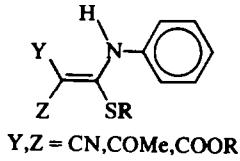


Y,Z = CN,COMe,COOR

2

Synthesis and rearrangements

Two classes of ketene derivatives have been prepared, the ketene derivatives **1** derived from *p*-methyl acetophenone and the ketene derivatives **2** derived from active methylene compounds.

In the first series, following known methods,[4,8-9] *p*-methyl acetophenone is reacted with CS_2 in the presence of a base and the dithioacid formed transformed into a tetrabutylammonium salt and subsequently alkylated. The monoalkylated products, the dithioesters, are most conveniently prepared by the ion-pair extraction technique as shown in a series of publications.[4-7] The thioamide is synthesized by reacting the dithioester with a secondary amine and by subsequently alkylating its Tl(I)-salt, the ketene derivative **1** is smoothly prepared. As the thallium salt does possess several possible alkylation cites, the position of the alkyl group had to be demonstrated. The NMR-spectrum of **1c** (R = Me) showed an one-proton singlet at δ 5·58 indicating an olefinic proton and IR showed a conjugated CO group from the absorption at 1600 cm^{-1}. The mass spectrum showed the presence of a methylthio group by the peaks at *m/e* 214(M-47) and *m/e* 47.

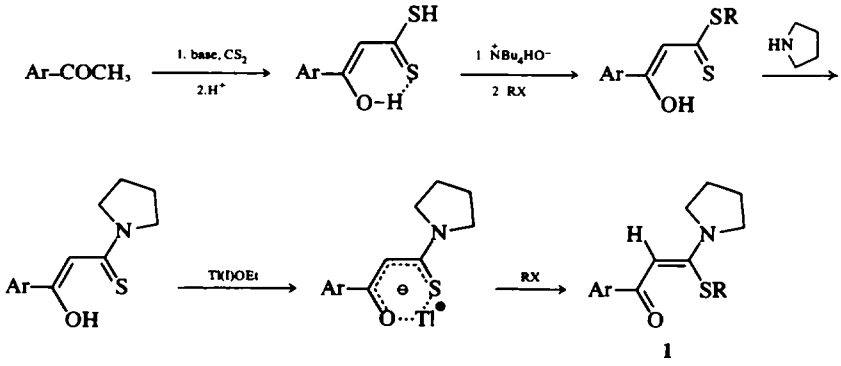
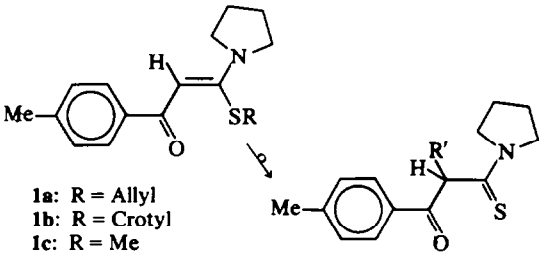


Fig 1.

Attempts were made to prepare the following ketene derivatives of type 1.



1a: R = Allyl
1b: R = Crotyl
1c: R = Me
1d: R = Et

3a: R = Allyl
3b: R = 1'-Methylallyl

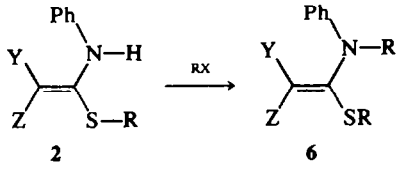
However, it was not possible to isolate the keteneacetals **1a** and **1b**, but only the rearrangement products **3**. The structures could be assigned from NMR spectroscopy. The NMR spectrum of **3a** indicated the disappearance of the olefinic proton, and the two-proton broad quartet at δ 2·28 demonstrated the presence of the structure element $CH\text{–}\underline{CH_2}\text{–}CH{=}CH_2$. In the NMR spectrum of **3b**, the number of olefinic protons had increased to 3, besides that the three-proton signal at δ 1·2 indicated a Me group adjacent to an asymmetric CH group.

When attempting to synthesize **1a**, it was also possible to isolate a moderate yield of the dialkylated ketene derivative **4** besides the main product **3a**. By assuming the rearrangement to take place during the reaction, the formation of **4** can be accounted for by a proton transfer from already formed **3a** to yet unalkylated thallium-salt, followed by alkylation of this new anion. (Fig 2)

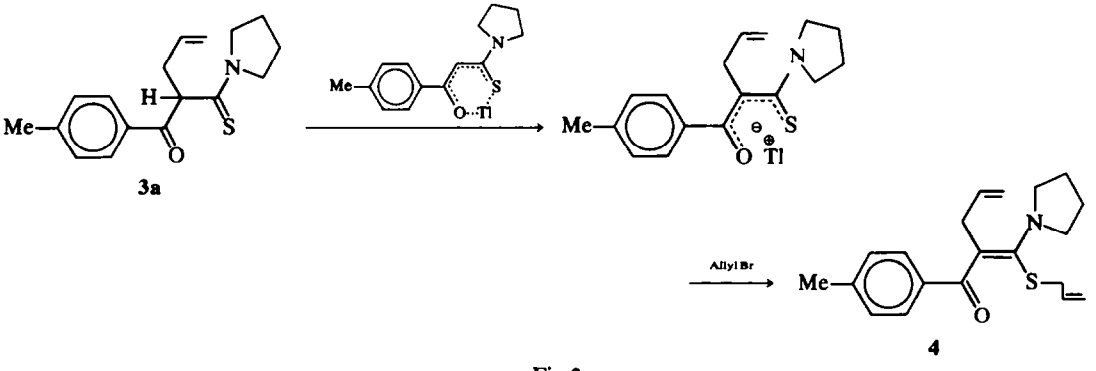
The second class of ketene derivatives was prepared by reacting an active methylene compound with a base and phenyl isothiocyanate to give the thioamide **5**.[9-16] Compound **5** could be alkylated in the presence of a base to the ketene derivative **2**.[14-15] (Fig 3, Table 1)

In the mass spectra of **2**, the dominating feature was the fragmentation of the alkoxycarbonyl or acetyl groups, but the presence of at least one of the fragments RS^+ and $M^+\text{–}SR$ showed the existence of the alkylthio group.

In several cases, small amounts of N,S-dialkylated keteneacetals **6** were isolated. As methylation of **2a** is known,[14] the introduction of the second allyl- or crotyl group must take place in an analogous way:

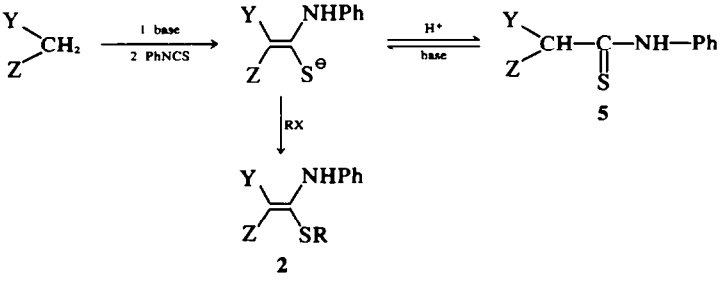


2 **6**



3a **4**

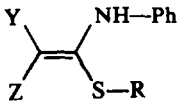
Fig 2.



2 **5**

Fig 3.

Table 1



2

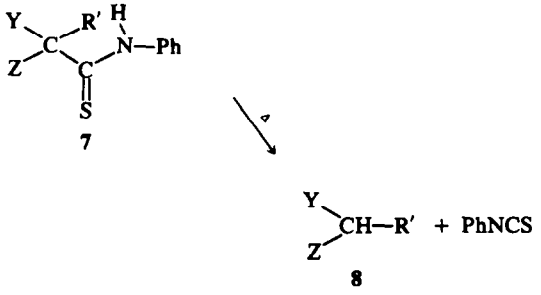
No.	Y	Z	R
2a	CN	COOMe	Me
2b	CN	COOMe	Allyl
2c	COOMe	COOMe	Allyl
2d	COOMe	COOMe	Crotyl
2e	COOEt	COOEt	Allyl
2f	COOEt	COOEt	Crotyl
2g	COMe	COOEt	Me
2h	COMe	COMe	Me
2j	H	COMe	Allyl

When R = allyl or crotyl, the reaction mixtures were distilled to give complex mixtures, which had to be separated further by chromatography. The products isolated included still unrearranged **2**, dialkylated product **6**, rearrangement product **7** and the cleavage products **8** and phenyl isothiocyanate.

The structure of **6** was supported by the fragments at *m/e* 146 (Ph–N–Crot) and M^+–146 in the mass spectrum of **6d** and the corresponding M-132 fragment from **6c**.

Besides evidence from IR, UV and NMR spectroscopy (loss of conjugation to ester-carbonyls, shortening of the chromophore and change of chemical shifts, especially of the allylic CH_2 groups) the assignment of the thioamide structure to **7** was supported by the mass spectra, which all had fragments corresponding to elimination of a sulphhydryl radical or H_2S besides fragments due to cleavage α to the thiocarbonyl group, as must be expected for thioamides.[17]

As distillation of the initial mixture took place at 140–170° (0·1–0·3 mmHg) and the thermal instability of the thioamide **7b** had been proved in a separate experiment, the formation of the cleavage products **8** and phenyl isothiocyanate can be accounted



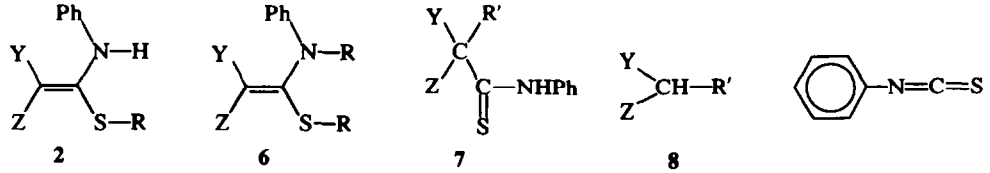
for by an internal hydrogen transfer and elimination of phenyl isothiocyanate.

Using t-butyl acetoacetate as active methylene compound and distilling the alkylated product (not isolated) in the presence of *p*-toluenesulphonic acid, elimination of isobutene and CO_2 took place besides rearrangement and cleavage of the rearranged product. Due to the very small yield of **7j** (0·9%), the structure was then confirmed by mass spectroscopy. α-Cleavage to the thiocarbonyl group gave the expected fragments at *m/e* 141 and 136 besides 97 (M^+-136). Cleavage α to the CO group gave *m/e* 218, 190 and 43 (MeCO). Elimination of the expected sulfhydryl radical[17] gave *m/e* 200 (4%) and expulsion of aniline gave *m/e* 93 ($C_6H_5NH_3^+$) as the base peak.

DISCUSSION

The formation of the rearrangement products obtained (**3** and **7**) can be accounted for by the normal

Table 2. Product distribution



2 6 7 8

Start Mat.	Y	Z	R	No	Yields of Products (in %) 2	6	7	8	PhNCS
5a	CN	COOMe	Allyl	b	1	5	—	11	12
5b	COOMe	COOMe	Allyl	c	27	6	28	—	—
5b	COOMe	COOMe	Crotyl	d	—	11	12	—	—
5c	COOEt	COOEt	Allyl	e	10	—	8	16	17
5c	COOEt	COOEt	Crotyl	f	5	—	9	—	—
—	Har CO_2tBu	COMe	Allyl	j	27	—	1	3	6

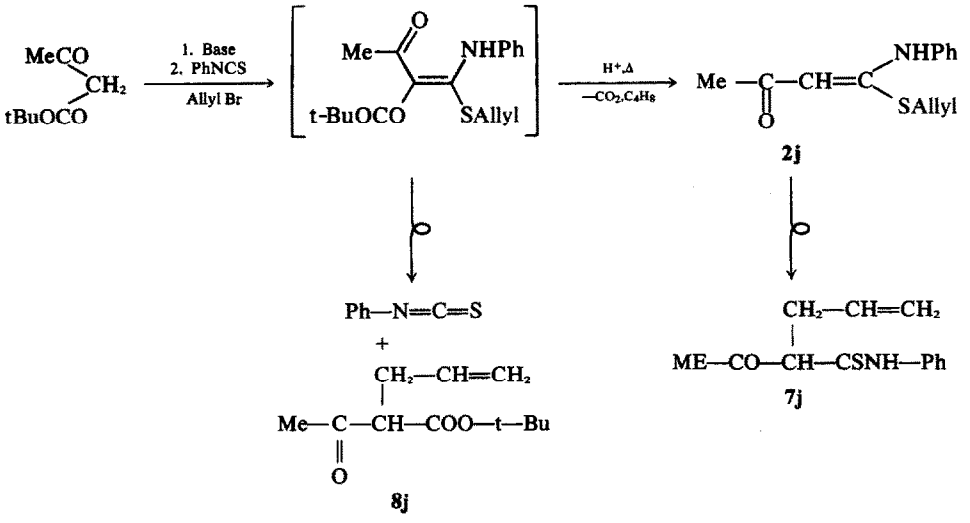


Fig 4.

thio-Claisen mechanism. When a crotyl group rearranged, the expected 1'-methylallyl compound was formed, in contradiction to rearrangements of some dicrotyl ketene-S,S-acetals.[5-7] Rearrangement products from the dialkylated ketene acetals **6** have not been observed.

In the ketene derivatives **1**, the thio-Claisen rearrangement is a smooth reaction, taking place during preparation of the ketene acetal, and giving up to 70% yield of rearrangement product and moderate yield of dialkylated product **4**. As long as no N–H bond is present, cleavage products are not observed.

The ketene derivatives **2**, derived from methyl cyanoacetate, dimethyl and diethyl malonates and t-butyl acetoacetate, do rearrange, but require conditions so severe (distillation at 150–170°) that decomposition of the rearrangement products takes place. Thus only small or moderate yields of the rearrangement product **7** are obtained and mostly small yields of the cleavage products **8** and phenyl isothiocyanate are isolated besides unrearranged **2** and dialkylation product **6**.

The influence of the arylamino group as compared with the alkylthio group is most apparent for the ketene acetals prepared from active methylene compounds. The tendency to undergo thio-Claisen rearrangement is reduced and a higher temperature is required.[5-7] Also the presence of the N–H-bond in the rearrangement product makes the formation of cleavage products possible and in this way further reduces the yields of rearranged products.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ at 60 Mc/s on a Varian A-60 spectrometer. The chemical shifts are expressed in ppm from TMS taken as 0·00 (δ-units). The UV spectra were recorded in $CHCl_3$ soln on a Bausch and Lomb 505 or a Perkin-Elmer 402 spectrophotometer. The IR spectra were recorded on a Beckman IR-18 spectrophotometer in $CHCl_3$ soln if not otherwise mentioned. The mass spectra were recorded on a CEC 21–104 operating at 70 eV using the direct inlet. Direct inlet temp 80–110°, ion source temp 240°. PLC was carried out on kiselgel $PF_{254+366}$ (Merck) support (20 × 40 cm and 3 mm thick). Column chromatography was carried out with kiselgel 60 (Merck). M.ps are uncorrected. Analyses were made by NOVO A/S, Copenhagen.

β-Hydroxy-p-methyl thiocinnamic pyrrolidide. This was synthesized according to a known procedure[8] from methyl β-hydroxy-*p*-methyl dithiocinnamate,[4] yield 74%, m.p. 136–137° (EtOH). (Found: C, 67·81; H, 7·99; N, 5·51; S, 12·69. $C_{14}H_{17}NOS$ requires: C, 67·99; H, 6·93; N, 5·66; S, 13·04%), NMR: 2·0 (m, 4H), 2·35 (s, 3H), 3·7 (m, 4H), 6·00 (s, 1H), 7·1–7·8 (m, 4H). IR: 715, 905, 1050, 1105, 1115, 1200, 1260, 1360, 1415, 1448, 1565, 1600, 2870 and 2970 cm^{-1}, UV: λ_{max} 333 nm, log ε = 4·06.

General synthesis of 3 - alkylthio - 1 - phenyl - 3 - pyrrolidino - 2 - propen - 2 - ones, **(1).** To β-hydroxy-*p*-methyl thiocinnamic pyrrolidide (0·747 g; 3 mmol) in 30 ml benzene thallium(I)ethoxide (0·823 g; 3·3 mmol) in 30 ml benzene was added. After stirring for 30 min the thallium salt was filtered off, added to 5 ml alkyl halide in 30 ml benzene, and refluxed overnight. After filtering off the thallium(I) halide and evaporation of the solvent, the crude product was isolated, which, when allyl or crotyl bromide were used as alkylating agent, had to be further purified by PLC.

3 - *Methylthio* - 3 - *pyrrolidino* - 1 - p - *tolyl* - 2 - *propenon* **(1c)**, yield 73%, m.p. 118–119° (EtOH). (Found: C, 68·32; H, 7·16; N, 5·26; S, 12·01; $C_{15}N_{19}NSO$ requires: C, 68·94; H, 7·33; N, 5·36; S, 12·25%), NMR: 1·8–2·1 (m, 4H), 2·37 (s, 3H), 2·47 (s, 3H), 3·4–3·7 (m, 4H), 5·58 (s, 1H), 7·1–7·9 (m, 4H), IR: 925, 1110, 1344, 1460, 1480, 1560, 1598, 2875 and 2980 cm^{-1}, UV: λ_{max} 258 nm (log ε = 3·91), λ_{max} 365 nm (log ε = 3·99). MS: *m/e* 261 (M^+, 4%), 260 (18), 231 (60), 214 (M-SMe, 18), 142 (22), 119 ($ArCO^+$, 100%), 91 (Ar^+, 96), 70 ($^+NR_2$, 96), 65 (52).

3 - *Ethylthio* - 3 - *pyrrolidino* - 1 - p - *tolyl* - 2 *propenon* **(1d)**. yield 95%. (Found: C, 69·72; H, 7·60; N, 4·93; S, 10·89; $C_{16}H_{21}NOS$ requires: C, 69·79; H, 7·69; N, 5·09; S,

11·62%); NMR: 1·30 (t, 3H), 1·8–2·2 (m, 4H), 2·33 (s, 3H), 3·00 (q, 2H), 3·4–3·8 (m, 4H), 5·68 (s, 1H), 7·1–7·9 (m, 4H); IR: 910, 1170, 1195, 1327, 1335, 1445, 1470, 1560, 1592, 2860 and 2960 cm^{-1}. UV: λ_{max} 259 nm (log ϵ = 3·91), λ_{max} 358 nm (log ϵ = 3·87), MS: *m/e* 275 (M^+, 33%), 247 (M–C_2H_4, 30), 214 (M–SEt, 18), 177 (247–C_4H_8N, 87), 156 (247–Ar, 41), 128 (156–CO, 68), 119 (ArCO, 100), 91 (99), 70 (97), 65 (51, 55 (52), 43 (54).

Attempt to prepare **1a**. Purified by PLC (10% EtOH in light petroleum) to give 70% **3a** and 17% **4**.

β - Hydroxy - α - allyl - p - methyl thiocinnamoyl pyrrolidide (**3a**), (Found: C, 70·97; H, 7·53; N, 4·74; S, 10·32; $C_{17}H_{21}NOS$ requires: C, 71·05; H, 7·37; N, 4·84; S, 11·14%); NMR: 1·8–2·2 (m, 4H), 2·35 (s, 3H), 2·8 (br.q., 2H), 3·5–4·0 (m, 4H), 4·50 (dd, 1H), 4·9–6·3 (m, 3H), 7·1–7·8 (m, 4H); IR: 1610, 1690, 2880 and 2990 cm^{-1}; UV: λ_{max} 267 nm, (log ϵ = 4·2).

3 - *Allylthio* - 3 - *pyrrolidino* - 2 - *allyl* - 1 - p - *tolyl* - 2 - *propenon* (**4**), (Found: C, 72·90; H, 7·90; $C_{20}H_{25}NOS$ requires: C, 73·36; H, 7·90%), NMR:c.1·3 (2H), 1·7–2·1 (m, 4H), 2·38 (s, 3H), 3·0–6·0 (12H), 7·1–8·0 (m, 5H); IR: 1160, 1255, 1445, 1605, 1685, 1745 and 2970 cm^{-1}; UV: λ_{max} 262 nm (log ϵ = 4·15).

β - Hydroxy - α - (1' - methylallyl) - p - methyl thiocinnamoyl pyrrolidide (**3b**). Purified by PLC (eluated twice with a mixture of 10% acetone, 50% benzene and 40% light petroleum), yield 37%. (Found: C, 71·65; H, 7·78; $C_{18}H_{23}NOS$ requires: C, 71·73; H, 7·69%); NMR: 1·2 (d, 3H), 1·8–2·2 (m, 4H), 1·37 (s, 3H), 4·6 (m, 1H), 3·3–4·1 (m, 4H), 4·8–6·3 (m, 3H), 7·1–7·9 (m, 4H); IR: 1445, 1610, 1690 and 2960 cm^{-1}; UV: λ_{max} 265 nm (log ϵ = 4·19). The thioamides **5a**, **5b** and **5c** were synthesized according to known methods.[9–11,14–16]

Synthesis of ketene derivatives **2** *and rearrangement products.* 25 mmol of **5** in 50 ml dry DMF were added dropwise to 26 mmol NaH in 30 ml DMF and stirred for 1 h. Then 10 ml alkyl bromide was added and stirring continued for 2 h. The mixture was then poured into water and extracted with ether. The collected ether phases were dried ($CaSO_4$), the ether evaporated and the product mixture distilled at 0·1 mmHg and further purified by chromatography. The identity of the decomposition products was proved by spectroscopic means and comparison with authentic samples.

Methyl 3 - *methylthio* - 3 - *anilino* - 2 - *cyano acrylate* (**2a**), was synthesized according to lit.,[14] MS: *m/e* 248 (M^+, 4%), 217 (M–OMe, 3%), 201 (M–MeS, 100%), 144 (201–MeOCO, 41%), 92 (PhNM, 6%), 77 (88%), 59 (MeOCO, 2%), 51 (24%), 47 (5%).

Allylation of **5a**. Purified by column chromatography (20–50% ether in light petroleum, then $CHCl_3$) to give 1·3% **2b**, 5% **6b**, 11%, 11% methyl allylcyanoacetate (**8b**), 12% phenyl isothiocyanate and 4% unchanged **5a**.

Methyl 3 - *allylthio* - 3 - *anilino* - 2 - *cyanoacetate* (**2b**), m.p. 63–64°. (Found: N, 10·20; S, 10·99; $C_{14}H_{14}N_2O_2S$ requires: N, 10·20; S, 11·67%); NMR: 3·35 (br.d, 2H), 3·83 (s, 3H), 4·9–6·0 (m, 3H), c.7·4 (m, 5H), 11·6 (1H); IR: 1250, 1370, 1425, 1480, 1550, 1580, 1655, 1740, 2200, 3000, 3300 cm^{-1}; UV: λ_{max} 319 nm (log ϵ = 3·96).

Methyl 3 - *allylthio* - N - *allyl* - N - *phenyl* - 3 - *amino* - 2 - *cyanoacetate* (**6b**); (Found: C, 64·36; H, 5·61; N, 9·08; S, 10·40; $C_{17}H_{18}N_2O_2S$ requires: C, 64·94; H, 5·77; N, 8·91; S, 10·18%); NMR: 2·95 (br.d, 4H), 3·74 (s, 3H), 5·6–6·0 (m, 6H), 6·8–7·5 (m, 5H); IR: 925, 985, 1090, 1215, 1420, 1470, 1585, 1620, 1740, 3000 cm^{-1}; UV: λ_{max} 251 nm (log ϵ = 3·63), λ_{max} 309 nm (log ϵ = 3·40).

Allylation of **5b**. Purified by column chromatography. Eluted by 20–100% ether in light petroleum to give 27% **2c**, 6% **6c** and 28% **7c**.

Methyl 3 - *allylthio* - 3 - *anilino* - 2 - *carbomethoxy acrylate* (**2c**), (Found: C, 59·38; H, 5·57; N, 4·30; S, 10·38; $C_{15}H_{17}NO_4S$ requires: C, 58·63; H, 5·58; N, 4·56; S, 10·41%); NMR: 3·27 (br.d, 2H, 3·78 (s, 6H), 5·0–5·9 (m, 3H), 7·2–7·9 (m, 5H), 12·0 (1H); IR: 1230, 1290, 1400, 1440, 1550, 1605, 1730, 1775, 2950, 3080 and 3200 cm^{-1}; UV: λ_{max} 315 nm, (log ϵ = 3·96); MS: *m/e* 307 (M^+, 28%), 274 (23), 248 (M–MeOCO, 48), 276 (M–OMe, 7), 234 (M–SAllyl, 5), 214 (M–$C_6H_5NH_2$, 15), 155 (68), 93 (14), 77 (100), 41 (Allyl, 34).

Methyl 3 - *allylthio* - N - *allyl* - N - *phenyl* - 3 - *amino* - 2 - *carbomethoxy acrylate* (**6c**), (Found: C, 61·28; H, 6·05; N, 3·61; S, 8·52; $C_{18}H_{21}NO_4S$ requires: C, 62·24; H, 6·10; N, 4·03; S, 9·31%); NMR: 3·0 (m, 4H), 3·7 (s, 6H), 4·7–6·4 (m, 6H), 6·9–7·8 (m, 5H); IR (film): 695, 763, 820, 920, 1240, 1365, 1440, 1490, 1570, 1600, 1630, 1740, 2955 and 3080 cm^{-1}; UV: λ_{max} 272 nm (log ϵ = 4·0); MS: *m/e* 347 (M^+, 0·29), 306 (M–All, 55), 273 (28), 215 (M–PhNAll, 12), 288 (M–MeOCO, 2), *m/e* 135 (φNCS, 43), 78 (100), 59 (19), 51 (28), 41 (70).

2, 2 - *Dicarbomethoxy* - 4 - *pentenoic thioanilide* (**7c**), (Found: C, 58·72; H, 5·78; N, 4·41; S, 9·25; $C_{15}H_{17}NO_4S$ requires: C, 58·63; H, 5·58; N, 4·56; S, 10·41%), m.p. 75–76°; NMR: 3·0 (br.d, 2H), 3·60 (s, 6H), 4·7–6·4 (m, 3H), c.7·3 (m, 5H); IR (film): 1495, 1750, 2940, 3010, 3070, 3300 cm^{-1}; UV: λ_{max} 314 nm (log ϵ = 3·99). MS: 307 (M^+, 54), 275 (M–MeOH, 41), 276 (M–MeO, 8), 214 (M–PhNH, 13), 136 ($PhNHCS^+$, 20) 77(100), 59 (53, MeOCO), 41 (All, 73).

Crotylation of **5b**. Purified by column chromatography (10% acetone, 40% light petroleum and 50% benzene) to give 11% **6d** and 12% **7d**.

Methyl 3 - *crotylthio* - N - *crotyl* - N - *phenyl* - 3 - *amino* - 2 - *carbomethoxy acrylate* (**6d**). (Found: C, 64·22; H, 6·80; N, 3·63; S, 8·94; $C_{20}H_{25}NO_4S$ requires: C, 63·98; H, 6·78; N, 3·73; S, 8·52%); NMR: 0·8–2·0 (m, 8H), 2·9 (m, 2H), 3·60 (s, 3H), 4·03 (s, 3H), 4·9–5·9 (m, 4H), 6·8–8·3 (m, 5H); IR (film): 1640, 1665, 1745, 2940 and 3020 cm^{-1}; UV: λ_{max} 273 nm (log ϵ = 4·42). MS: *m/e* 375 (M^+, 13), 344 (M–OMe, 11), 321 (M–C_4H_6, 61), 289 (M–SCrot, 13), 235 (321–SCrot, 100), 202 (82), 228 (M–PhNCrot, 11), 146 (PhNCrot, 74), 104 (42), 87 (CrotS, 43), 77 (72), 59 (45), 55 (93).

Methyl 2, 2 - *dicarbomethoxy* - 3 - *methyl* - 4 - *pentenoic thioanilide* (**7d**), (Found: C, 60·24; H, 5·84; N, 4·34; S, 9·11; $C_{16}H_{19}NO_4S$ requires: C, 59·80; H, 5·96; N, 4·36; S, 9·58%); NMR: 1·7 (br.d, 3H), 3·3 (m, 1H), 3·58 (s, 6H), 4·4 (m, 1H), 5·3–5·8 (m, 3H), 7·1–7·4 (m, 5H); IR (film): 1440, 1500, 1720, 2945 and 3020 cm^{-1}; UV: λ_{max} 297 nm (log ϵ = 3·83), λ_{max} 352 nm (log ϵ = 3·65); MS: *m/e* 321 (M^+, 36), 290 (M–OMe, 48), 257 (290–SH, 38), 202 (257–MeAll, 88), 171 (202–OMe), 105 (Ph–Migr., 84), 77 (100), 55 (100), 43 (43).

Allylation of **5c**. Purified by PLC (eluted twice in 10% ether in light petroleum) after distillation to give 10% **2e**, 8% **7e**, 16% diethyl allylmalonate[18] (**8e**) and 17% phenyl isothiocyanate.

Ethyl 3 - *anilino* - 3 - *allylthio* - 2 - *carboethoxy acrylate* (**2e**), m.p. 58–59°. (Found: C, 60·74; H, 6·27; N, 4·48; S, 10·35; $C_{17}H_{21}NO_4S$ requires: C, 60·87; H, 6·32; N, 4·18; S, 9·56%); NMR: 1·4 (2t, 6H), 3·82 (br.d, 2H), 4·5 (2q, 4H), 5·0–6·5 (m, 3H), 7·2–8·3 (m, 5H), 13·18 (1H); IR: 1220, 1277, 1360, 1385, 1422, 1460, 1495, 1572, 1595, 1635, 1660, 1740, 2990 and 3070 cm^{-1}; UV: λ_{max} 272 nm (log ϵ = 4·57).

2, 2 - *Dicarboethyl pent* - 4 - *enoic thioanilide* (**7e**), m.p.

75–76°. (Found: C, 60·80; H, 6·56; N, 3·98; S, 8·84; $C_{17}H_{21}NO_4S$ requires: C, 60·87; H, 6·32; N, 4·18; S, 9·56%); NMR: 1·27 (t, 6H), 3·8 (br.d, 2H), 4·28 (q, 4H), 5·0–6·0 (m, 3H), 7·2–7·9 (m, 5H), 13·18 (1H); IR: 1200, 1400, 1608, 1730, 1765, 2980 and 3200 cm^{-1}; UV: λ_{max} 314 nm (log ϵ = 3·96); MS: *m/e* 349 (M^+, 14), 304 (M–OMe, 52), 257 (M–PhNH, 48), 224 (257–SH, 100), 105 (Ph-migr., 47), 77 (93), 55 (MeAll, 68), 45 (16), 43 (34).

Crotylation of **5c**. Purified by PLC (20% ether in light petroleum) to give 5% **2f** and 9% **7f**.

Ethyl 3 - *anilino* - 3 - *crotylthio* - 2 - *carboethoxy acrylate* (**2f**), (Found: C, 67·95; H, 7·37; N, 4·51; $C_{18}H_{23}NO_4S$ requires: C, 68·11; H, 7·32; N, 4·41%); NMR: 1·15 (t, 6H), 2·37 (br.d, 2H), c.3·35 (br.t, 3H), 4·05 (q, 4H), 4·4 (1H), 5·0–6·0 (m, 2H), 7·0–7·5 (m, 5H); IR: 1100, 1205, 1375, 1500, 1715, 2940 and 2980 cm^{-1}; UV: λ_{max} 295 nm (log ϵ = 3·92); MS: *m/e* 349 (M^+, 44), 334 (M–Me, 3), 320 (M–Et, 10), 216 (258–CH: CHMe, 38), 258 (M–PhNH, 11), 190 (18), 144 (216-C_2H_4-CO_2, 85), 104 ($PhN\hat{C}H$, 27), 93 104 ($PhN\hat{C}H$, (74), 87 (CrotS, 21), 55 (Crot, 100), 45 (45).

2, 2 - *Dicarboethoxy* - 3 - *methyl* - 4 - *pentenoic thioanilide* (**7f**), m.p. 64–65°. (Found: C, 68·10; H, 6·48; N, 4·72; S, 10·68; $C_{18}H_{23}NO_4S$ requires: C, 68·11; H, 7·32; N, 4·41; S, 10·10%); NMR: 1·48 (t, 6H), 1·7 (br.d, 3H), 2·9 (m, 1H), 4·0–5·9 (m, 3H), 4·53 (q, 4H), 6·9–8·3 (m, 5H), 13·20 (1H); IR: 1210, 1490, 1565, 1590, 1625, 1655, 1735 and 2980 cm^{-1}; UV: λ_{max} 271 nm, (log ϵ = 4·61); MS: *m/e* 349 (M^+, 16), 304 (M–OEt, 56), 257 (M–NHPh, 54), 230 (29), 135 (PhNCS, 31), 77 (100).

Ethyl 3 - *anilino* - 3 - *methylthio* - 2 - *acetyl acrylate* (**2g**). Ethyl acetoacetate (13·0 g; 0·10 mole) in 30 ml DMF were added dropwise to 0·11 mole NaH in 50 ml DMF at 0–5°. When no more H_2 was evolved, stirring was continued for 20 min and thin phenyl isothiocyanate (13·5 g; 0·10 mole) were added. Stirring was continued for 1 hr, and 10 ml MeI were added. After stirring for 1 h more, the mixture was poured into water, extracted with ether, and the collected ether phases dried ($CaSO_4$). After evaporation of the ether, 3·68 g (13%) **2g** were obtained. (Found: C, 60·07; H, 6·08; N, 4·96; S, 11·54; $C_{14}H_{17}NO_3S$ requires: C, 60·21; H, 6·14; N, 5·02; S, 11·48%); NMR: 1·26 (t, 3H, *J* = 7 cs), 2·28 (s, 3H), 2·35 (s, 3H), 3·48 (s, 3H), 4·13 (q, 2H, *J* = 7 cs), 7·2–7·5 (5H); IR: 685, 935, 1060, 1345, 1590, 1695, 2970 cm^{-1}; UV λ_{max} 251 nm (log ϵ = 4·05), λ_{max} 251 nm (log ϵ = 4·05), λ_{max} 311 nm (log ϵ = 3·78), λ_{max} 347 nm (log ϵ = 3·60); MS: *m/e* 279 (M^+, 6%), 231 (M–MeSH, 62%), 186 (M–$PhNH_2$, 30), 143 (185–CH_3CO, 100), 77 (80%), 51 (11%), 47 (8), 43 (32).

1 - *Anilino* - 2 - *acetyl* - 1 - *methylthio but* - 1 - *en* - 3 - *on* (**2h**). Synthesis analogous to **2g** starting from acetylacetone, yield 73%, m.p. 72–73°. (Found: C, 62·34; H, 6·12; N, 5·40; S, 12·66; $C_{13}H_{15}NO_2S$ requires: C, 62·34; H, 6·07; N, 5·62; S, 12·84%); NMR: 2·07 (s, 6H), 3·13 (s, 3H), 6·6–7·3 (m, 5H), 16·25 (s, 1H); IR: 680, 930, 1395, 1475, 1590, 2970 cm^{-1}; UV: λ_{max} 251 nm (log ϵ = 4·07), λ_{max} 284 nm (log ϵ = 4·04); MS; *m/e* 249 (M^+, 5%), 202 (M–SMe, 100%), 160 (202–CH_2: C : 0·26%), 144 (202–CH_3CO–Me, 29%), 18 (160–CH_2CO, 24%), 77 (93%), 51 (35%), 47 (SMe, 7%), 43 (CH_3CO^+, 74%).

Synthesis of **2j**, **7j** *and* **8j**. t-Butyl acetoacetate (15·8 g; 0·1 mole) in 10 ml THF were added to t-BuOK (12·4 g; 0·11 mole) in 65 ml THF at 0° and stirred for 10 min. Then phenyl isothiocyanate (13·5 g; 0·10 mole) in 25 ml THF were added dropwise and stirring continued for 15 min at 0°. Finally allyl bromide (10 ml) were added and stirring continued for 0·5 h. Then the mixture was poured into water, extracted with ether and the organic phases dried ($CaSO_4$). The ether was evaporated, 0·5 g *p*-toluenesulphonic acid added and then the mixture heated at 10 mmHg to eliminate CO_2 and isobutene. Afterwards distillation was performed at 0·1–0·3 mmHg. The distillate was purified by column chromatography (ether in light petroleum) to give **2j** (6·16 g; 27%) **8j**[19] (0·48 g; 2·5%) **7j** (0·21 g; 0·9%) and (0·81 g; 6% phenyl isothiocyanate).

4 - *Allylthio* - 4 - *anilino* - 3 - *buten* - 2 - *one* (**2j**), (Found: C, 66·81; H, 6·41; N, 6·23; S, 13·16; $C_{14}H_{15}NOS$ requires: C, 66·93; H, 6·48; N, 6·01; S, 13·74%); NMR: 2·30 (s, 3H), 2·8 (br.d, 2H), 4·24 (1H), 4·9–6·0 (m, 3H), 7·2–7·8 (m, 5H), 10·2 (1H); IR (film): 910, 1400, 1490, 1530, 1710, 2980, 3045 and 3240 cm^{-1}; UV: λ_{max} 247 nm (log ϵ = 3·76) λ_{max} 279 nm (log ϵ = 3·88), λ_{max} 310 nm (log ϵ = 3·89); MS: *m/e* 233 (M^+, 54%), 218 (M–Me, 8), 190 (M–CH_3CO, 100%), 160 (M–SAll, 6%), 97 (190–$PhNH_2$, 17%), 77 (15), 51 (7), 43 (30), 41 (4).

2-*Allyl acetothioacetanilid* (**7j**), NMR: 2·41 (s, 3H), 2·7 (br.q, 2H), 3·62 (t, 1H, *J* = 7), 4·9–6·1 (m, 3H), 7·0–7·7 (m, 5H), 8·9 (br.s, 1H); IR: 690, 924, 1160, 1512, 1613, 1650, 1705, 1732, 2900, 3005 and 3440 cm^{-1}; UV: λ_{max} = 248 nm (log ϵ = 4·01), λ_{max} = 314 nm (log ϵ = 3·61); MS; *m/e* 233 (M^+, 3), 218 (M–Me, 30), 200 (M–SH, 47), 190 (M–MeCO, 12), 157 (M–C_6H_5, 2), 141 (M–PhNH, 4), 136 ($PhNHCS^+$, 4), 97 (218–$PhNH_2$–CO, 6), 93 ($PhNH_2^+$, 100), 77 (14), 66 (93-C_2H_3, 7), 65 (93–HCN, 11), 53 (97–CS, 6), 51 (5), 43 (43).

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