CYCLIZATION AND OXIDATION OF N-SUBSTITUTED PHENYL-N'-(2-METHYL-3-PHENYLPROPENOYL)THIOUREAS

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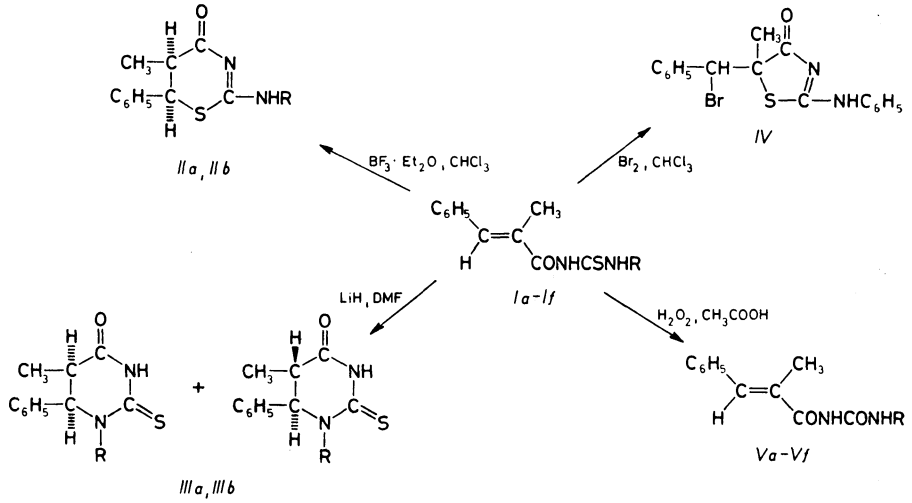
The synthesis of 1,3-thiazines, 2-thiouracils and ureas from N-substitutited phenyl-N'-(2-methyl-3-phenylpropenoyl)thioureas by intramolecular cyclization or oxidation under various conditions is described. The structure of products was verified by IR, ^{1}H NMR and mass spectral evidence.

Thioureas cyclize to afford five- or six-membered heterocycles interesting also as biologically active compounds[1-4]. This fact motivated us to examine cyclization of N-substituted phenyl-N'-(2-methyl-3-phenylpropenoyl)thioureas leading either to derivatives of 1,3-thiazine or to 2-thiouracil according to conditions employed. In addition also oxidation of the above-mentioned thioureas to ureas and their Hugershoff reaction[5] were investigated. In continuation of our previous paper, concerning analogous cyclizations of thioureas with 2-cyano-3-phenylpropenoyl or 2,3-diphenylpropenoyl groupings in the molecule[6,7] we investigated the influence of an electron-donating methyl group in position 2 of this system on regio- and stereoselectivity of these reactions.

N-Substituted phenyl-N'-(2-methyl-3-phenylpropenoyl)thioureas *Ia*–*If* were synthesized by addition of 4-substituted anilines to (*E*)-2-methyl-3-phenylpropenoyl isothiocyanate. The respective thioureas were crystallized from ethanol and characterized by spectral (IR, ^{1}H NMR) methods. In addition to characteristic absorption bands and resonance signals, shift of the quartet associated with the olefinic proton at δ 7·51–7·57 ppm is very important. Comparison with the calculated values[8,9] (7·53 for an (*E*)-isomer and 6·87 for a (*Z*)-one) configuration (*E*) was assigned to compounds prepared.

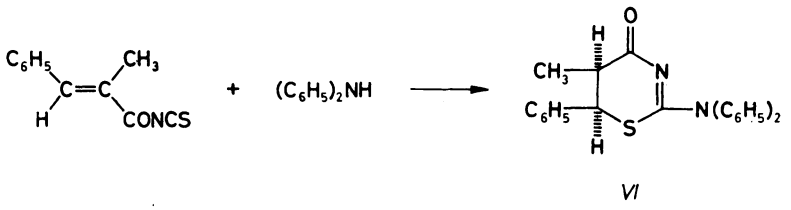
Due to an ambident character of the thiocarbamoyl grouping in the thioureas synthesized, cyclization through sulfur to yield 1,3-thiazines, or through nitrogen to afford 2-thiouracils took place according to conditions applied. *Cis*-2-(4-substituted phenyl)amino-6-phenyl-5-methyl-5,6-dihydro-4*H*-1,3-thiazine-4-ones (*IIa* and *IIb*, Scheme 1) were obtained by an intramolecular cyclization of the respective thioureas *Ia*, *Ib* under catalysis of boron trifluoride. Reaction of diphenylamine with 2-methyl-3-phenylpropenoyl isothiocyanate led directly to *cis*-2-diphenylamino-

-6-phenyl-5-methyl-5,6-dihydro-4*H*-1,3-thiazin-4-one (*VI*) even at 10°C in benzene, or alternatively under reflux (Scheme 2).



In formulae *I*–*III*, *V* *a*, R = C_6H_5 *b*, R = 4-$CH_3C_6H_4$ *c*, R = 4-BrC_6H_4 *d*, R = 4-ClC_6H_4 *e*, R = 4-$CH_3OC_6H_4$ *f*, R = 2-CH_3-4ClC_6H_3

SCHEME 1



SCHEME 2

The intramolecular cyclization of derivatives *Ia* and *Ib* in N,N-dimethylformamide in the presence of lithium hydride furnished the mixture of *cis*- and *trans*-6-phenyl-1--(4-substituted)-5-methyl-2-thiouracils *IIIa* and *IIIb* (Scheme 2); these were not succeded to separate by chromatography. The mixture of *cis*- and *trans*-2-thiouracils *IIIa* and *IIIb* could also be prepared by heating thiourea in absolute ethanol in the presence of triethylamine. As found, the *cis*- to *trans*-isomers ratio depended on the molecular ratio of thiourea to triethylamine (Table I).

Taking this finding in account we tried to utilize the Dimroth rearrangement of our 1,3-thiazines to 2-thiouracils employing methods from our previous papers[6,7]. The Dimroth rearrangement of *IIa* and *IIb* in the presence of lithium hydride in N,N-dimethylformamide, or in the presence of triethylamine in absolute ethanol afforded the same products *IIIa* and *IIIb* like cyclization of thioureas *Ia* and *Ib* at the same reaction conditions. A suitable method for evidencing and identifying the *cis*- and *trans*-isomers of *cis*-1,3-thiazines *IIa* and *IIb* and the mixture of *cis*- and *trans*-2-thiouracils *IIIa* and *IIIb* was shown to be vicinal coupling constants ^3J(AB) of protons H-5, H-6 in the ^{1}H NMR spectra measured by the INDOR technique in the CW regime. Derivatives revealing a higher coupling constant are *trans*-isomers and vice versa, in line with[10,11]. The ratio of geometric isomers in crystallized mixtures *IIIa* and *IIIb* was estimated by means of integrated intensities –CH—CH– in the ^{1}H NMR spectra. 2-Thiouracils could be distinguished from 1,3-thiazines by IR spectra too, basing upon stretching vibration of carbonyl groups. With 2-thiouracils possessing a –NHCO– grouping a noticeable shift of absorption of the carbonyl group was observed when compared with 1,3-thiazines possessing a C=N—C=O grouping. The structure of compounds under study was also verified by mass spectrometry.

Following differences and analogy were observed when preparing 1,3-thiazine and 2-thiouracil derivatives bearing a methyl group (electron donor) or a cyano or phenyl groups (electron acceptors) in position 2 of the 3-phenylpropenoyl residue under the same reaction conditions: (i) The cyano group (a strong electron-acceptor) binds the solvent during crystallization (benzene, ethanol) what was proved by IR and ^{1}H NMR spectroscopies and by thermal analysis[6]. Phenyl or methyl substituted derivatives did not show this property. (ii) Papers[6,7] and also this contribution displayed that reaction of 2-substituted-3-phenylpropenoyl isothiocyanates with diphenylamine under various conditions always afforded 1,3-thiazine systems

TABLE I

Effect of the amount of triethylamine on the *cis* to *trans* ratio of *IIIa*

Triethylamine[a]	% *cis*[b]	% *trans*[b]
0.5	70	30
1·0	60	40
2·0[c]	10	90

[a] Mol per 1 mol of *Ia*; [b] as calculated from the ^{1}H NMR spectra; [c] a 10—100 fold excess of triethylamine does not influence the *cis* to *trans* ratio of *IIIa*.

without isolation of the corresponding thiourea. (iii) The proposed mechanism of intramolecular cyclization is in accordance with the literature[12].

Examination of the Hungershoff reaction of thiourea *Ia* with bromine in chloroform showed that the addition proceeded at the ethylene multiple bond to give 5-(α-bromobenzyl)-2-phenylamino-5-methylthiazolin-4-one (*IV*) (Scheme 1); its structure was deduced from the ^{1}H NMR and mass spectral measurements. Singlets of CH and CH_3 protons at δ 5·34 and 1·96 ppm, respectively, indicated ceasing the double bond; signals of the olefinic CH protons and the doublet belonging to CH_3 protons of thiourea *Ia* lie at δ 7·51 and 2·18 ppm, respectively.

Pesticide properties of ureas are more promising than those of thioureas, and that is why we oxidized thioureas *Ia*–*If* to ureas *Va*–*Vf* (Scheme 1). It is known[13–15] that various oxidation agents can be used for this purpose. Yield of oxidation of *Ia* with potassium ferricyanide in an alkaline medium was 35%, that with mercury oxide in acetone under reflux 54% and that with hydrogen peroxide in acetic acid 70%. Since the latter is most effective, it was applied for the remaining thioureas *Ib*–*If*, too. The ureas *Va*–*Vf* are little soluble in organic solvents, and therefore, their structures were corroborated by elemental analyses and IR spectra in KBr pellets.

The pesticide effect was so far tested with derivatives *IIa* and *IIIa* and no herbicide or antifungal properties were found. The pre-emergent in vivo experiments with barley infected with *Erisipe graminis* showed a strong phytotoxicity.

EXPERIMENTAL

The infrared spectra were taken with a Specord IR 74 (Zeiss, Jena) apparatus in chloroform (compounds *Ia*–*If*, *IIa*, *IIb*, *IIIa*, *IIIb*, *IVa*, *VI*) or in KBr pellets (*Va*–*Vf*; wavelengths in cm^{-1}). The ^{1}H and ^{13}C NMR spectra of deuterochloroform solutions containing tetramethylsilane as internal reference were recorded with Tesla BS 487A (80 MHz) and Tesla BS 567 (25·15 MHz) apparatuses, respectively; the reported values are in ppm on the δ scale, coupling constants in Hz. The mass spectra were measured with an AEI MS 9025 (Manchester) spectrometer at 70 eV ionization energy. The reaction course was monitored by thin-layer chromatography on Silufol (Kavalier, Czechoslovakia) sheets. (*E*)-2-Methyl-3-phenylpropenoyl isothiocyanate was synthesized according to ref.[16].

General Procedure for Preparation of N-Substituted Phenyl-N′-(2-methyl-3-phenylpropenoyl)thioureas *Ia*–*If*

Substituted aniline (30 mmol) in benzene (30 ml) was added to a stirred solution of (*E*)-2-methyl-3-phenylpropenoyl isothiocyanate (6·10 g, 30 mmol) in benzene (30 ml). The separated precipitate was filtered off, dried and crystallized from ethanol.

N-*Phenyl*-N′-(2-*methyl*-3-*phenylpropenoyl*)*thiourea* (Ia). Yield 59%, m.p. 134–135°C. IR spectrum: 3 425 (NH), 1 664 (C=O), 1 585 (C=C), 1 496 (NHCS). ^{1}H NMR spectrum: 1·18 d, 3 H (CH_3, J = 1·41); 7·51 q, 1 H (CH, J = 1·41); 7·40 m, 5 H (Ar–H); 7·13–7·85 m, 5 H

(Ar–H); 8·91 s, 1 H (NH). For $C_{16}H_{17}N_2OS$ (269·4) calculated: 68·69% C, 5·44% H, 9·45% N; found: 68·96% C, 5·36% H, 9·60% N.

N-(4-*Methylphenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*thiourea* (Ib). Yield 58%, m.p. 170 to 171°C. IR spectrum: 3 430 (NH), 1 665 (C=O), 1 587 (C=C). 1 508 (NHCS). ^{1}H NMR spectrum: 2·19 d, 3 H (CH_3, J = 1·4); 2·36 s, 3 H (CH_3-Ar); 7·53 q, 1 H (CH, J = 1·4); 7·40 m, 5 H (Ar-H); 7·21 and 7·54 dd, 4 H (Ar-H); 8·96 s, 1 H (NH). For $C_{18}H_{18}N_2OS$ (310·4) calculated: 69·64% C, 5·84% H, 9·02% N; found: 69·78% C, 5·94% H, 9·10% N.

N-(4-*Bromophenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*thiourea* (Ic). Yield 39%, m.p. 164 to 165°C. IR spectrum: 3 420 (NH), 1 660 (C=O), 1 580 (C=C), δ 480 (NHCS). ^{1}H NMR spectrum: 2·19 d, 3 H (CH_3, J = 1·4); 7·58 q, 1 H (CH, J = 1·4); 7·36 m, 5 H (Ar-H); 7·38 and 7·64 dd, 4 H (Ar-H); 9·10 s, 1 H (NH). For $C_{17}H_{15}BrN_2OS$ (375·3) calculated: 54·40% C, 4·02% H, 7·46% N; found: 54·56% C, 4·12% H, 7·46% N.

N-(4-*Chlorophenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*thiourea* (Id). Yield 51%, m.p. 117 to 118°C. IR spectrum: 3 420 (NH), 1 663 (C=O), 1 477 (NHCS). ^{1}H NMR spectrum: 2·18 d, 3 H (CH_3, J = 1·4); 7·57 q, 1 H (CH, J = 1·4); 7·42 m, 5 H (Ar-H); 7·36 d and 7·67 dd, 4 H (Ar-H); 8·96 s 1 H (NH). For $C_{17}H_{15}ClN_2OS$ (330·8) calculated: 61·71% C, 4·57% H, 8·46% N; found: 61·84% C, 4·62% H, 8·63% N.

N-(4-*Methoxyphenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*thiourea* (Ie). Yield 49%, m.p. 149 to 150°C. IR spectrum: 3 420 (NH), 1 660 (C=C), 1 477 (NHCS). ^{1}H NMR spectrum: 2·19 d, 3 H (CH_3, J = 1·4); 3·83 s, 3 H CH_3O-Ar); 7·56 q, 1 H (CH, J = 1·4); 7·44 m, 5 H (Ar-H); 6·97 to 7·58 m, 4 H (Ar-H); 8·94 s, 1 H (NH). For $C_{18}H_{18}N_2O_2S$ (326·4) calculated: 66·23% C, 5·56% H, 8·58% N; found: 66·38% C, 6·78% H, 8·69% N.

N-(4-*Chloro*-2-*methylphenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*thiourea* (If). Yield 31%, m.p. 155–156°C. IR spectrum: 3 400 (NH), 1 660 (C=O), 1 595 (C=C), 1 475 (NHCS). ^{1}H NMR spectrum: 2·19 d, 3 H (CH_3, J = 1·4); 2·31 s, 3 H (CH_2-Ar); 7·58 q, 1 H (CH, J = 1·4); 7·40 m, 5 H (Ar-H); 7·12 and 7·86 m, 3 H (Ar-H); 9·06 s, 1 H (NH). For $C_{18}H_{17}ClN_2OS$ (344·9) calculated: 62·68% C, 4·96% H, 8·12% N; found: 62·83% C, 5·02% H, 8·30% N.

General Procedure for Preparation of *cis*-2-(4-Substituted Phenyl)-amino-6-phenyl-3-methyl-5,6-dihydro-4*H*-1,3-thiazin-4-ones *IIa*, *IIb*

To a solution of thiourea *Ia* or *Ib* (5 mmol) in chloroform (15 ml) boron trifluoride etherate (1·25 ml, 10 mmol) was introduced. The mixture was neutralized after 30 min with a 4%-aqueous sodium hydrogen carbonate (35 ml, 10 mmol). The chloroform layer was separated, dried with magnesium sulfate, the solvent was distilled off and the residue was crystallized from a suitable solvent.

cis-2-*Phenylamino*-6-*phenyl*-5-*methyl*-5,6-*dihydro*-4H-1,3-*thiazin*-4-*one* (IIa). Yield 80%, m.p. 143–144°C (cyclohexane). IR spectrum: 3 362 (NH), 1 684 (C=O), 1 615 (C=N). ^{1}H NMR spectrum: 1·13 d, 3 H (CH_3); 3·15 m, 1 H (CH); 4·58 d, 1 H (CH, J(AB) = 4·2); 7·25 m, 10 H (Ar-H). Mass spectrum, m/z (%): 296 (M^+, 28), 118 (34), 85 (50), 56 (60), 28 (100). For $C_{17}H_{16}N_2OS$ (296·4) calculated: 68·89% C, 5·44% H, 9·45% N; found: 68·99% C, 5·52% H, 9·56% N.

cis-2-(4-*Methylphenyl*)*amino*-6-*phenyl*-5-*methyl*-5,6-*dihydro*-4H-1,3-*thiazin*-4-*one* (IIb). Yield 71%, m.p. 140–141°C (tetrachloromethane). IR spectrum: 3 340 (NH), 1 690 (C=O), 1 620 (C=N). ^{1}H NMR spectrum: 1·24 d, 3 H (CH_3); 2·34 s, 3 H (CH_3); 3·15 m, 1 H (CH); 4·64 d, 1 H (CH, J(AB) = 4·12); 7·18 m, 9 H (Ar-H). For $C_{18}H_{18}N_2OS$ (310·4) calculated: 69·64% C, 5·84% H, 9·02% N; found: 69·78% C, 5·92% H, 9·13% N.

Mixture of *cis*- and *trans*-6-Phenyl-1-(4-Substituted Phenyl)-5-methyl-2-thiouracils (*IIIa*, *IIIb*)

A. Lithium hydride (0·2 g, 25 mmol) was added to a solution of the respective thiourea *Ia*, *Ib* (2 mmol) or thiazine *IIa*, *IIb* in N,N-dimethylformamide (15 ml) and the mixture was allowed to stand at room temperature for 5 days. Water (20 ml) was added to the mixture, which was in turn neutralized with dilute (2 : 1) hydrochloric acid. The precipitate thus formed was filtered off and crystallized from ethanol. From thioureas *Ia* and *Ib* compounds *IIa* and *IIIb* were obtained in 47 and 68% yields, and from thiazines *IIa* and *IIb* compounds *IIIa* and *IIIIb* in 30 and 38% yields, respectively.

B. Triethylamine (1·01 g, 10 mmol) was added to a solution of thiourea *Ia* or thiazine *IIa* in ethanol (50 ml). The mixture was refluxed for 10 h and left to stand at an ambient temperature for 24 h. The solid was filtered off, dried and crystallized from ethanol. From thiourea *Ia* and thiazine *Ia* and thiazine *IIa* the respective yields of *IIIa* were 30 and 34%.

Mixture of cis- *and* trans-1,6-*diphenyl*-5-*methyl*-2-*thiouracils* (IIIa). M.p. 207—209°C. IR spectrum: 3 334 (NH), 1 695 (C=O). ^{1}H NMR spectrum: 7·25 m, 10 H (C_6H_5); 8·97 s, 1 H (NH); *cis*-isomer: 3·11 m, 1 H (CH); 4·75 d, 1 H (CH, *J*(AB) = 2·41); 3·53 m, 1 H (CH); *trans*-isomer: 4·81 d, 1 H (CH, *J*(AB) = 7·32). Mass spectrum, *m*/*z* (%): 296 (M^+, 72), 118 (100), 92 (18), 28 (87). For $C_{17}H_{16}N_2OS$ (296·4) calculated: 68·89% C, 5·44% H, 9·45% N; found: 68·97% C, 5·52% H, 9·62% N.

Mixture of cis- *and* trans-6-*phenyl*-1-(4-*methylphenyl*)-5-*methyl*-2-*thiouracils* (IIIb). M.p. 174—176°C. IR spectrum: 3 392 (NH), 1 715 (C=O). ^{1}H NMR spectrum: 2·31 s, 3 H (CH_3); 7·14 m, 9 H (Ar-H); 8·84 s, 1 H (NH); *cis*-isomer: 1·05 d, 3 H (CH_3); 2·98 m, 1 H (CH); 4·73 d, 1 H (CH, *J*(AB) = 2·35); *trans*-isomer: 1·60 d, 3 H (CH_3); 3·46 m, 1 H (CH); 4·78 d, 1 H (CH, *J*(AB) = 7·27). For $C_{18}H_{18}N_2OS$ (310·4) calculated: 69·64% C, 5·84% H, 9·02% N; found: 69·78% C, 5·97% H, 9·24% N.

5-(α-Bromobenzyl)-2-phenylamino-5-methylthiazolin-4-one (*IVa*)

Bromine (0·48 g, 3 mmol) was added dropwise to a stirred solution of thiourea *Ia* (0·81 g, 3 mmol) in chloroform (20 ml) at room temperature. After 1 h the mixture was left to stand for 24 h, the solvent was evaporated and the solid was crystallized from methanol. Yield 36%, m.p. 156 to 158°C. IR spectrum: 3 382 (NH), 1 650 (C=O), 1 590 (C=N). ^{1}H NMR spectrum: 1·96 s, 3 H (CH_3); 5·34 s, 1 H (CH); 7·40 m, 10 H (Ar-H); 8·39 s, 1 H (NH). Mass spectrum, *m*/*z* (%): 374 (M^+, 58), 376 (M^+, 60), 294 (39), 205 (37), 169 (100). For $C_{17}H_{15}BrN_2OS$ (375·3) calculated: 54·41% C, 4·03% H, 7·46% N; found: 54·62% C, 4·09% H, 7·53% N.

N-Substituted Phenyl-N′-(2-methyl-3-phenylpropenoyl)thioureas (*Va*—*Vf*)

Acetic acid (12 ml) containing 30%-hydrogen peroxide (8 ml) was added slowly to thiourea *Ia*—*If* (4 mmol) dissolved in glacial acetic acid (8 ml). The precipitate separated during 30 min was filtered off, washed with water and crystallized from ethanol.

N-*Phenyl*-N′-(2-*methyl*-3-*phenylpropenoyl*)*urea* (Va). Yield 70%, m.p. 184—185°C. IR spectrum: 3 190 (NH), 1 650 and 1 690 (C=O), 1 580 (C=C). For $C_{17}H_{16}N_2O_2$ (280·3) calculated: 72·84% C, 5·75% H, 9·99% N; found: 72·96% C, 5·83% H, 10·08% N.

N-(4-*Methylphenyl*)-N′-(2-*methyl*-3-*phenylpropenoyl*)*urea* (Vb).
Yield 76%, m.p. 176—177°C. IR spectrum: 3 224 (NH), 1 660 and 1 690 (C=O), 1 597 (C=C).

For $C_{18}H_{18}N_2O_2$ (294·4) calculated: 73·44% C, 6·16% H, 9·51% N; found: 73·56% C, 6·21% H, 9·61% N.

N-(4-*Bromophenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*urea* (Vc). Yield 74%, m.p. 193–194°C. IR spectrum: 3 223 (NH), 1 655 and 1 692 (C=O), 1 575 (C=C). For $C_{17}H_{15}BrN_2O_2$ (395·2) calculated: 56·83% C, 4·20% H, 7·79% N; found: 56·92% C, 4·28% H, 7·86% N.

N-(4-*Chlorophenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*urea* (Vd). Yield 63%, m.p. 198–199°C. IR spectrum: 3 215 (NH), 1 657 and 1 688 (C=O), 1 598 (C=C). For $C_{17}H_{15}Cl_2NO_2$ calculated: 64·86% C, 4·80% H, 8·90% N; found: 64·99% C, 4·92% H, 8·98% N.

N-(4-*Methoxyphenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*urea* (Ve). Yield 69%, m.p. 176–177°C. IR spectrum: 3 210 (NH), 1 660 and 1 690 (C=O), 1 598 (C=C). For $C_{18}H_{18}N_2O_3$ (310·4) calculated: 69·66% C, 5·84% H, 9·02% N; found: 69·78% C, 5·97% H, 9·21% N.

N-(4-*Chloro*-2-*methylphenyl*)-N'-(2-*methyl*-3-*phenylpropenoyl*)*urea* (Vf). Yield 70%, m.p. 199–200°C. IR spectrum: 3 220 (NH), 1 655 and 1 690 (C=O), 1 587 (C=C). For $C_{18}H_{17}Cl.N_2O_2$ (328·8) calculated: 65·76% C, 5·21% H, 8·52% N; found: 65·84% C, 5·18% H, 8·61% N.

cis-2-Diphenylamino-6-phenyl-5-methyl-5,6-dihydro-4*H*-1,3-thiazin-4-one (*VI*)

A. Diphenylamine (0·85 g, 5 mmol) dissolved in benzene (5 ml) was added dropwise to a stirred and in an ice-bath cooled solution of (*E*)-2-methyl-3-phenylpropenoyl isothiocyanate (1·02 g, 5 mmol) in benzene (30 ml). The mixture was allowed to stand at an ambient temperature for 12 h, the crystals were filtered off, dried and crystallized from tetrachloromethane; yield 53%.

B. Diphenylamine (0·85 g, 5 mmol) in benzene (5 ml) was introduced to a stirred solution of (*E*)-2-methyl-3-phenylpropenoyl isothiocyanate (1·02 g, 5 mmol) in benzene (30 ml). The mixture was refluxed for 90 min, cooled and left to stand for 12 h at room temperature. The separated crystals were filtered off, dried and recrystallized from tetrachloromethane; yield 88%, m.p. 172–173°C. IR spectrum: 1 655 (C=O), 1 530 (C=N). ^{1}H NMR spectrum: 1·11 d, 3 H (CH_3); 2·98 m, 1 H (CH); 4·55 d, 1 H (CH, J(AB) = 4·8); 7·35 m, 15 H (C_6H_5). ^{13}C NMR spectrum: 12·21 q (CH_3); 39·83 d and 50·13 d (CH); 167·82 s and 179·88 s (C=O, C=N). For $C_{23}H_{20}N_2OS$ (372·5) calculated: 74·16% C, 5·41% H, 7·52% N; found: 74·45% C, 5·69% H, 7·83% N.

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