SYNTHESIS OF 2,2,4-TRISUBSTITUTED 2*H*-1,3-OXAZETES FROM ACYL ISOTHIOCYANATES

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Received May 13th, 1978

Reaction of acyl isothiocyanates with amines, methanol or methanethiol afforded addition products which on treatment with lithium hydride in dimethylformamide and subsequent alkylation with methyl iodide, cyclised immediately to give 2,2,4-trisubstituted 2*H*-1,3-oxazetes which represent a new type of heterocycles. Under identical conditions, N-phenyl-N′-cinnamoylthioureas and N-phenyl-N′-3-(2-furyl)-acryloylthioureas afforded S-methyl N-acylmonothiocarbamates whereas N-phenyl-N′-acetylthiourea gave N-phenyl-N′-acetyl-S-methylisothiourea. The structure of the obtained compounds was confirmed by their IR, ^{1}H-NMR and mass spectra.

In our previous studies we investigated nucleophilic addition reactions of α,β-unsaturated acyl isothiocyanates with NaHS which, depending on substituents, gave rise to either 6-substituted-4-oxo-2-thioxo-perhydro-1,3-thiazines or 5-benzylidene--1-oxo-2-thioxo-1,3-thiazolidine[1,2].

This paper concerns addition reactions of acyl isothiocyanates *I* with other nucleophiles, namely with amines, methanol and methanethiol, performed with the aim to obtain intermediates suitable for further cyclisation. We found that the obtained addition products (N-acylthioureas *IIa*–*IId*, O-methyl monothiocarbamates *IIe* and methyl dithiocarbamates *IIf*) react with lithium hydride in dimethylformamide to give the lithium salts *A*. These on treatment with methyl iodide are converted into unstable intermediates *B* which undergo an immediate cyclisation to hitherto undescribed four-membered heterocycles of the 2*H*-1,3-oxazete type (*III*, Scheme 1; Table I).

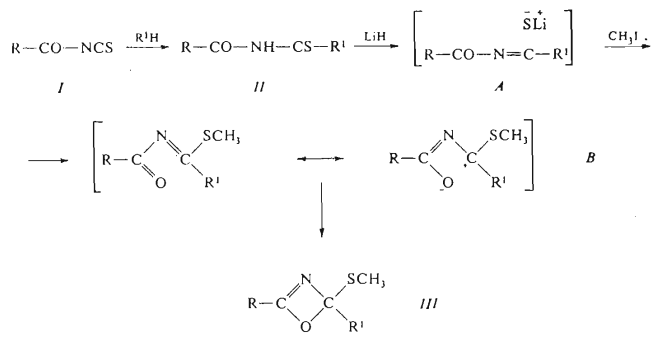
Of the three theoretically possible types of oxazete heterocycles, only 4*H*-1,2-oxazete and 1,2-oxazet-3-ene derivatives have hitherto been described. Berndt[3] prepared 4,4-di-tert-butyl-3-methyl-4*H*-1,2-oxazet N-oxide (*IV*) by intramolecular cyclisation of 3-tert-butyl-4,4-dimethyl-2-nitro-2-pentene. Later, together with Wieser[4], he prepared substituted 1,2-oxazet N-oxides by reaction of 1,1-di-tert-butylallenes with N_2O_4, followed by cyclisation of the arising dinitro compounds. The same authors[5] synthesized 4,4,3-trisubstituted 4*H*-1,2-oxazetes (*V*) by thermal cyclisation of α,β-unsaturated nitro compounds or by action of dilute sulfuric acid on ammonium 3-tert-

TABLE I

Synthesized 2,2,4-Trisubstituted 2*H*-1,3-Oxazetes

Compound	Formula (mol. w.)	M.p., °C (solvent)[a]	Yield, %	Calculated/Found		
				% C	% H	% N
III1c	$C_{11}H_{14}N_2OS$ (222·3)	61–63 (DMFA–water)	64	59·25 59·39	6·34 6·12	12·60 12·47
III2a	$C_9H_{10}N_2OS$ (194·3)	112–114 (cyclohexane)	73	55·62 55·85	5·14 5·36	14·51 14·38
III2b	$C_{10}H_{12}N_2OS$ (208·3)	63–64 (DMFA–water)	60	57·66 57·63	5·80 5·99	13·44 13·20
III2c	$C_{16}H_{16}N_2OS$ (284·4)	87–89 (light petroleum)	86	69·68 69·83	5·66 5·41	9·85 10·02
III2d	$C_{15}H_{14}N_2OS$ (269·3)	102–104 (light petroleum)	38	66·88 66·78	5·27 5·01	10·40 10·25
III2e	$C_{10}H_{10}NO_2S$ (209·3)	37–39 (DMFA–water)	70	57·39 57·31	5·29 5·30	6·69 6·99
III2f	$C_{10}H_{11}NOS_2$ (225·3)	41·5–43·5 (DMFA–water)	73	53·30 53·24	4·92 5·07	6·21 6·17
III3a	$C_{11}H_{12}N_2OS$ (220·3)	46–48 (n-hexane)	59	59·98 59·69	5·49 5·54	12·72 12·60
III3b	$C_{12}H_{14}N_2OS$ (234·3)	102 (n-heptane)	47	61·51 61·74	6·02 6·13	11·96 11·74
III3c	$C_{18}H_{18}N_2OS$ (310·2)	68–69 (cyclohexane)	73	69·65 69·40	5·84 5·82	9·02 9·23
III3e	$C_{12}H_{13}NO_2S$ (235·3)	60–61 (n-hexane)	85	61·25 61·03	5·57 5·61	5·92 6·21
III3f	$C_{13}H_{13}NOS_2$ (251·4)	86–87 (n-hexane)	53	57·34 57·05	5·21 5·23	5·57 5·70
III4a	$C_9H_{10}N_2O_2S$ (210·3)	68–69 (cyclohexane)	80	51·41 51·42	4·78 4·86	13·32 13·03
III4b	$C_{10}H_{12}N_2O_2S$ (224·3)	48–50 (light petroleum)	70	53·55 53·81	5·39 5·69	12·44 12·21
III4c	$C_{16}H_{16}N_2O_2S$ (300·4)	51–53 (ethanol–water)	73	63·97 63·78	5·36 5·53	9·32 9·17
III4e	$C_{10}H_{11}NO_3S$ (225·3)	69–70 (cyclohexane)	83	53·80 54·05	4·90 4·78	6·18 6·38
III4f	$C_{10}H_{11}NO_2S_2$ (241·3)	56–58 (cyclohexane)	71	49·77 49·61	4·59 4·32	5·80 6·01

[a] DMFA dimethylformamide.



$R = CH_3$ (*1*), C_6H_5 (*2*), C_6H_5—CH=CH (*3*), 2-furyl—CH=CH (*4*)
$R^1 = NH_2$ (*a*), $NHCH_3$ (*b*), $NHCH_2C_6H_5$ (*c*), C_6H_5 (*d*), OCH_3 (*e*), SCH_3 (*f*)

SCHEME 1

-butyl-4,4-dimethyl-2,3-dinitro-2-pentanide and treatment of the obtained oxime with sodium methoxide under formation of $NaNO_2$. Jermakova and coworkers[6] obtained 3,4-difluoro-2-trifluoromethyl-1,2-oxazet-3-ene (*VI*) by reaction of iron pentacarbonyl with 3,4-difluoro-2-trifluoromethyl- and 3-fluoro-2-trifluoromethyl--4-chloro-1,2-oxazetidine.

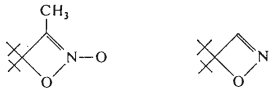
In the case of α,β-unsaturated acyl isothiocyanates we considered also the possibility of an intramolecular cyclisation to six-membered thiazine derivatives which would arise by nucleophilic attack by sulfur atom at the β-carbon of the ethylenic bond in the intermediate *A*. However, we isolated 2*H*-1,3-oxazetes as the sole reaction products. Our present synthesis represents thus a simple method for preparation of the mentioned compounds in high yields. Whereas in the synthesis of N-acyl-thioureas and O-methyl monothiocarbamates we used a direct addition of amines or methanol to the corresponding acyl isothiocyanates, methyl dithiocarbamates could preferably be prepared by addition of NaHS to acyl isothiocyanates in the presence of methyl iodide. In the further reaction step, treatment with lithium hydride afforded the lithium salts already at room temperature, except the compounds *II4b* and *II4c* which required heating to 50°C. The intermediates *B*, formed by methylation of the lithium salts, are stabilized by intramolecular cyclisation and separate upon dilution of the reaction mixture with water.

TABLE II

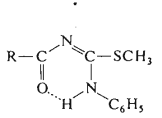
Spectral Data for 2,2,4-Trisubstituted 2*H*-1,3-Oxazetes

Compound	IR, cm^{-1}			^{1}H-NMR, ppm		Mass spectra
	ν(C=N)	ν(C=C)	$\delta(SCH_3)$	δ(CH=CH)	δ(ArH)	*m/e* (rel. int., %)
III1c	1 565	—	2·46	—	7·33	—
III2a	1 576	—	2·55	—	7·38—8·18	194 (100), 179 (11), 147 (27), 105 (100), 51 (71), 47 (13), 44 (5), 28 (42)
III2b	1 572	—	2·58	—	7·36—8·19	—
III2c	1 570	—	2·65	—	7·36—8·28	—
III2d	1 559	—	2·55	—	3·35	—
III2e	1 648	—	2·40	—	7·48—8·11	—
III2f	1 646	—	2·48	—	7·45—8·08	—
III3a	1 577	1 642	2·50	6·67; 7·70	7·37	220 (95), 205 (13), 173 (71), 131 (100), 103 (100), 51 (53), 47 (52), 44 (71), 32 (15), 28 (100)
III3b	1 574	1 641	2·52	6·60; 7·67	7·35	—
III3c	1 570	1 640	2·58	6·67; 7·75	7·32	—
III3e	1 618	1 642	2·37	6·37; 7·82	7·39	—
III3f	1 612	1 643	2·55	6·37; 7·67	7·37	—
III4a	1 575	1 632	2·48	6·48; 7·45	6·43—7·43	210 (100), 195 (10), 163 (76), 121 (100), 93 (26), 65 (100), 47 (34), 44 (86), 39 (79), 32 (9), 28 (100)
III4b	1 570	1 641	2·51	6·49; 7·44	6·43—7·44	224 (100), 209 (4), 121 (100), 93 (26), 65 (100), 47 (34), 44 (86) 39 (79), 32 (9), 28 (100)
III4c	1 568	1 643	2·51	6·58; 7·45	6·43—7·45	—
III4e	1 612	1 632	2·36	6·44; 7·43	6·45—7·48	225 (100), 210 (4), 178 (50), 121 (100), 93 (19), 65 (78), 47 (26), 44 (38), 39 (78), 32 (13), 28 (92)
III4f	1 615	1 638	2·58	6·49; 7·41	6·46—7·49	241 (100), 194 (7), 121 (100), 93 (16), 65 (100), 47 (35), 44 (32) 39 (95), 32 (8), 28 (56)

In the case of S-methylisothioureas, no cyclic products were isolated from the derivatives *VII*. We assume that this failure to cyclise to the corresponding 1,3-oxazetes is caused by stabilisation with an intramolecular hydrogen bond. The compound *VIIa* could be isolated whereas compounds *VIIb* and *VIIc* upon dilution of the reaction mixture with water underwent hydrolysis to the corresponding dicarbonyl derivatives *VIII*.

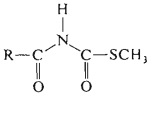


IV *V* *VI*



VII

R = CH_3(*a*), C_6H_5—CH=CH(*b*), 2-furyl-CH=CH(*c*)



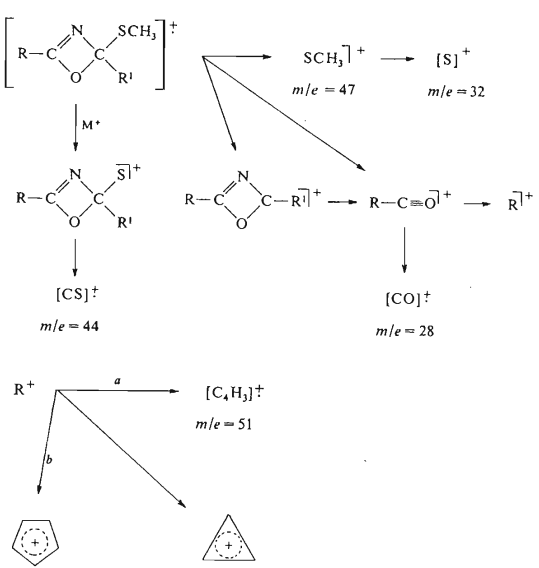
VIII

R = C_6H_5—CH=CH(*a*), 2-furyl-CH=CH(*b*)

The IR, ^{1}H-NMR and mass spectra of the synthesized products are in accord with their proposed structure (Table II). The IR spectra of 1,3-oxazetes display characteristic bands ν(C=N) at 1570–1648 cm^{-1}. No carbonyl bands were observed. Spectra of the derivatives synthesized from α,β-unsaturated acyl isothiocyanates exhibit absorption bands at about 1640 cm^{-1}, proving thus that the C=C bonds have been preserved. The ^{1}H-NMR spectra of all derivatives show signals due to SCH_3 groups (δ = 2·37–2·58) and to aromatic protons; the derivatives with styryl and furylvinyl moieties exhibit also two doublets of *trans*-ethylenic protons (J_{AB} = 16 Hz).

An unequivocal proof of the 1,3-oxazete structure is given by the mass spectra. High intensity of the molecular ions indicates stability of the studied compounds. The fundamental general fragmentation paths are given in Scheme 2.

The *m/e* values of the molecular ions as well as the results of elemental analyses confirm the expected summary formulas of the prepared compounds. On the basis of the found summary formulas we calculated the number of cycles and double bonds[7] which is in accord with the proposed 1,3-oxazete structure.



a, R = C_6H_5, C_6H_5—CH=CH
b, R = 2-furyl—CH=CH

SCHEME 2

EXPERIMENTAL

Acetyl isothiocyanate[8], benzoyl isothiocyanate[9], *trans*-cinnamoyl isothiocyanate[10], *trans*-3-(2-furyl)acryloyl isothiocyanate[11], N-phenyl-N'-acetylthiourea[12], N-benzyl-N'-acetylthiourea[13], N-methyl-N'-benzoylthiourea[14], benzoylthiourea[15], N-benzyl-N'-benzoylthiourea[15], N-phenyl-N'-benzoylthiourea[15], O-methyl-N-benzoylmonothiocarbamate[15], cinnamoylthiourea[16], and N-phenyl-N'-cinnamoylthiourea[16] were prepared according to the literature.

N-Substituted N'-Acylthioureas (*II3b,c*; *II4a—d*)

A stirred and cooled solution of acyl isothiocyanate (0·023 mol) in benzene (40 ml) was saturated with gaseous ammonia or treated with aniline (0·025 mol) or benzylamine (0·025 mol). In the case of methylamine, its 30% aqueous solution (0·025 mol) was added to a solution of acyl isothiocyanate (0·023 mol) in acetone (40 ml). The corresponding thiourea precipitated immediately,

in the case of methylamine upon dilution with twice the volume of water. The product was filtered, washed with light petroleum (or in the last case with water), dried and crystallized from an appropriate solvent.

N-*Methyl*-N′-*cinnamoylthiourea* (II3b), yield 33%, m.p. 210–211°C (benzene). For $C_{11}H_{12}N_2OS$ (220·3) calculated: 59·97% C, 5·49% H, 12·72% N; found: 60·21% C, 5·53% H, 12·64% N. IR spectrum, cm^{-1} (KBr): ν(C=O) 1673, ν(C=C) 1628, γ(CH=CH) 928. ^{1}H-NMR spectrum ($CDCl_3$): 11·12 and 10·75 (singlets, —NH—), 7·75 and 6·95 (doublets, —CH=CH—, J_{AB} = = 16 Hz), 7·37 (multiplet, C_6H_5), 3·12 (doublet, CH_3, J = 4 Hz). N-*Benzyl*-N′-*cinnamoylthiourea* (II3c), yield 84%, m.p. 192–193°C (ethanol). For $C_{17}H_{16}N_2OS$ (296·4) calculated: 68·89% C, 5·44% H, 9·45% N; found: 68·57% C, 5·82% H, 9·30% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3417, ν(C=O) 1697, ν(C=C) 1629, γ(CH=CH) 982. ^{1}H-NMR spectrum ($CDCl_3$): 11·28 (singlet, —NH—), 7·73 and 6·97 (doublets, —CH=CH—, J_{AB} = 16 Hz), 7·35 (multiplet, C_6H_5), 4·90 (doublet, —CH_2—, J = 6 Hz).

3-(2-*Furyl*)*acryloylthiourea* (II4a), yield 64%, m.p. 232–233°C (ethanol–water). For $C_8H_8N_2O_2S$ (196·2) calculated: 48·96% C, 4·10% H, 14·27% N; found: 49·13% C, 4·01% H, 14·06% N. IR spectrum, cm^{-1} ($CHCl_3$): $\nu_{as}(NH_2)$ 3490, $\nu_s(NH_2)$ 3419, ν(C=O) 1688, ν(C=C) 1630, ν(NHCS) 1510, ν(skeletal, furan) 1023, γ(CH=CH) 972. ^{1}H-NMR spectrum ($CDCl_3$–hexadeuteriodimethyl sulfoxide): 11·00 (singlet, —NH—), 9·98 and 8·80 (singlets, NH_2), 7·45 and 6·69 (doublets, —CH=CH—, J_{AB} = 16 Hz).

N-*Methyl*-N′-3-(2-*furyl*)*acryloylthiourea* (II4b), yield 67%, m.p. 193–195°C (ethanol–water). For $C_9H_{10}N_2O_2S$ (210·3) calculated: 51·41% C, 4·79% H, 13·32% N; found: 51·52% C, 4·70% H, 13·39% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3419, $\nu_{as}(CH_3)$ 2946, ν(C=O) 1689, ν(C=C) 1629, ν(skeletal, furan) 1021, γ(CH=CH) 987. ^{1}H-NMR spectrum ($CDCl_3$–hexadeuteriodimethyl sulfoxide): 11·06 (singlet, —NH—), 9·91 (quartet, —NH—, J = 5 Hz), 7·45 and 6·70 (doublets, —CH=CH—, J_{AB} = 16 Hz), 3·13 (doublet, CH_3, J = 5 Hz). N-*Benzyl*-N′-3-(2-*furyl*)*acryloylthiourea* (II4c), yield 64%, m.p. 164–166°C (ethanol). For $C_{15}H_{14}N_2O_2S$ (286·3) calculated: 62·91% C, 4·92% H, 9·78% N; found: 62·80% C, 5·08% H, 9·90% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3419, ν(C=O) 1680, ν(C=C) 1628, ν(NHCS) 1505, ν(skeletal, furan) 1023, γ(CH=CH) 970. ^{1}H-NMR spectrum ($CDCl_3$): 11·33 and 11·05 (singlets, —NH—), 7·53 and 6·73 (doublets, —CH=CH—, J_{AB} = 16 Hz), 7·38 (singlet, C_6H_5), 4·91 (doublet, —CH_2—, J = 5 Hz). N-*Phenyl*-N′-3-(2-*furyl*)*acryloylthiourea* (II4d), yield 71%, m.p. 145–146°C (methanol–water). For $C_{14}H_{12}N_2O_2S$ (272·3) calculated: 61·73% C, 4·44% H, 10·29% N; found: 61·65% C, 4·52% H, 10·12% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3413, ν(C=O) 1678, ν(C=C) 1629, ν(NHCS) 1530, ν(skeletal, furan) 1022, γ(—CH=CH—) 969. ^{1}H-NMR spectrum ($CDCl_3$): 11·01 (singlet, NH), 7·50 and 6·70 (doublets, —CH=CH—, J_{AB} = 16 Hz).

O-Methyl N-Acylmonothiocarbamates *II3e*, *II4e*

Acyl isothiocyanate (0·014 mol) in methanol (25 ml) was refluxed for 45 min, cooled and carefully diluted with cold water (200 ml). The arising precipitate was filtered, washed with water, dried and crystallized from a suitable solvent.

O-*Methyl* N-*cinnamoylmonothiocarbamate* (II3e), yield 78%, m.p. 132°C (ethanol–water). For $C_{11}H_{11}NO_2S$ (221·3) calculated: 59·71% C, 5·01% H, 6·33% N; found: 59·58% C, 5·38% H, 6·01% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3420, ν(C=O) 1722, ν(C=C) 1631, γ(CH=CH) 982. ^{1}H-NMR spectrum ($CDCl_3$): 9·45 (singlet, —NH—), 7·82 and 6·98 (doublets, —CH=CH—, J_{AB} = 16 Hz), 7·40 (multiplet, C_6H_5), 4·12 (singlet, CH_3). O-*Methyl* N-3-(2-*furyl*)*acryloylmonothiocarbamate* (II4e), yield 67%, m.p. 117–118°C (methanol–water). For $C_9H_9NO_3S$ (211·2) calculated: 51·17% C, 4·29% H, 6·63% N; found: 51·35% C, 4·23% H, 6·43% N. IR spec-

trum, cm^{-1} ($CHCl_3$): ν(NH) 3411, $\nu_{as}(CH_3)$ 2963, $\nu_s(CH_3)$ 2861, ν(C=O) 1683 and 1722, ν(C=C) 1632, ν(NHCS) 1510, ν(skeletal, furan) 1021, γ(CH=CH) 982. ^{1}H-NMR spectrum ($CDCl_3$): 11·13 (singlet, —NH—), 7·48 and 6·70 (doublets, —CH=CH—, J_{AB} = 16 Hz), 4·10 (singlet, CH_3).

Methyl N-Acyldithiocarbamates *II2f, 3f, 4f*

A solution of NaSH (0·03 mol) in methanol (40 ml) was added to a stirred and cooled mixture of acyl isothiocyanate (0·022 mol), methyl iodide (0·03 mol) and dimethylformamide (40 ml). The mixture was diluted with water (200 ml), the precipitate collected on filter, washed with water, dried and crystallized from aqueous ethanol.

Methyl N-*benzoyldithiocarbamate* (II2f), yield 86%, m.p. 132—134°C. For $C_9H_9NO_2S$ (211·3) calculated: 51·15% C, 4·29% H, 6·62% N; found: 51·26% C, 4·08% H, 6·81% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3400, $\nu_{as}(CH_3)$ 2930, ν(C=O) 1688 and 1700, ν(NHCS) 1468. ^{1}H-NMR spectrum ($CDCl_3$): 11·33 (singlet, —NH—), 7·95 and 7·48 (multiplets, C_6H_5), 2·63 (singlet, CH_3). Preparation of this compound by another route is described in the literature[17,18]. *Methyl* N-*cinnamoyldithiocarbamate* ((II3f), yield 73%, m.p. 178—180°C. For $C_{11}H_{11}NOS_2$ (237·3) calculated: 55·68% C, 4·67% H, 5·90% N; found: 55·73% C, 4·95% H, 5·81% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3389, ν(C=O) 1696, ν(C=C) 1632, γ(CH=CH) 982. ^{1}H-NMR spectrum ($CDCl_3$): 12·30 (singlet, —NH—), 7·85 and 6·95 (doublets, —CH=CH—, J_{AB} = 16 Hz), 7·40 (multiplet, C_6H_5), 2·55 (singlet, CH_3).

Methyl N-3-(2-*furyl*)*acryloyldithiocarbamate* (II4f), yield 60%, m.p. 147—149°C. For $C_9H_9NO_2S_2$ (227·4) calculated: 47·55% C, 3·98% H, 6·16% N; found: 47·48% C, 4·07% H, 6·18% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3389, $\nu_{as}(CH_3)$ 2930, ν(C=O) 1695, ν(C=C) 1629, ν(NHCS) 1469, ν(skeletal, furan) 1021, γ(CH=CH) 971. ^{1}H-NMR spectrum ($CDCl_3$): 12·05 (singlet, NH), 7·51 and 6·71 (doublets, —CH=CH—, J_{AB} = 16 Hz), 2·58 (singlet, CH_3).

2,2,4-Trisubstituted 2*H*-1,3-Oxazetes *III1c, III2a—f, III3a,b,d—f, III4a,b,d—f*

The corresponding N-acylthiourea (or O-methyl monothiocarbamate or methyl dithiocarbamate) (0·005 mol) was added under stirring and cooling with water to a suspension of lithium hydride (0·005 mol) in dimethylformamide (20 ml). The mixture was stirred until it became homogeneous (10—60 min), methyl iodide (0·005 mol) was added and the stirring was continued for 45 min. The stirred mixture was poured into cold water (100 ml), the crystalline precipitate filtered, washed with water, dried and crystallized from an appropriate solvent. In the case of the compounds *III4b* and *III4c* the reaction with lithium hydride was carried out at 45—50°C (Table I and II).

N-Acetyl-N′-phenyl-S-methylisothiourea (*VIIa*)

This compound was obtained by reaction of N-phenyl-N′-acetylthiourea (0·005 mol) with lithium hydride (0·005 mol) followed by methyl iodide (0·005 mol) in dimethylformamide (20 ml), analogously as described in the preceding experiment. Yield 40%, m.p. 78—80°C (light petroleum). For $C_{10}H_{12}N_2OS$ (208·3) calculated: 57·66% C, 5·80% H, 13·44% N; found: 57·69% C, 5·73% H, 13·43% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3395, $\nu_{as}(CH_3)$ 2941, ν(C=O) 1723, ν(C=N) 1613. ^{1}H-NMR spectrum ($CDCl_3$): 7·18 (multiplet, C_6H_5), 2·37 (singlet, CH_3), 2·06 (singlet, CH_3).

S-Methyl N-Acylmonothiocarbamates *VIIIa,b*

The title compounds were prepared by reaction of N-phenyl-N'-acylthiourea (0·005 mol) with lithium hydride (0·005 mol) and methyl iodide (0·005 mol) under conditions described for the preparation of 1,3-oxazetes.

S-*Methyl* N-*cinnamoylmonothiocarbamate* (VIIIa), yield 71%, m.p. 137—138°C (n-heptane). For $C_{11}H_{11}NO_2S$ (212·3) calculated: 60·24% C, 5·22% H, 6·59% N; found: 60·54% C, 5·37% H, 6·58% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3404, ν(CO—NH—$CO_{in\ phase}$) 1712, ν(CO—NH—$CO_{out\ of\ phase}$) 1668, ν(C=C) 1634, γ(CH=CH) 982. ^{1}H-NMR spectrum ($CDCl_3$): 11·05 (singlet, —NH—), 7·75 and 6·80 (doublets, —CH=CH—, J_{AB} = 16 Hz), 7·40 (multiplet, C_6H_5), 2·30 (singlet, CH_3).

S-*Methyl* N-3-(2-*furyl*)*acryloylmonothiocarbamate* (VIIIb), yield 80%, m.p. 136—138°C (cyclohexane). For $C_9H_9NO_3S$ (120·3) calculated: 53·71% C, 4·68% H, 6·71% N; found: 53·57% C, 4·50% H, 6·96% N. IR spectrum, cm^{-1} ($CHCl_3$): ν(NH) 3405, $\nu_{as}(CH_3)$ 2942, ν(CO—NH—$CO_{in\ phase}$) 1705, ν(CO—NH—$CO_{out\ of\ phase}$) 1665, ν(C=C) 1632, ν(skeletal, furan) 1022, γ(CH=CH) 975. ^{1}H-NMR spectrum ($CDCl_3$): 11·03 (singlet, —NH—), 7·49 and 6·65 (doublets, —CH=CH—, J_{AB} = 16 Hz), 2·31 (singlet, CH_3).

Spectral Measurements

Infrared absorption spectra of the synthesized compounds were measured in chloroform in the region 800—3 500 cm^{-1} on a double-beam spectrophotometer UR-20 (Zeiss,) calibrated by a polystyrene foil. The ^{1}H-NMR spectra were taken in deuteriochloroform on a Tesla BS 487A instrument (80 MHz), using tetramethylsilane as internal standard. Mass spectral measurements were carried out on an MS 902 S (AEI Manchester) spectrometer (direct inlet, 70 eV, ionisation chamber temperature: *III2a* 60°C, *III3a* 55°C, *III4a* 50°C, *III4b,e* 30°C, *III4f* 45°C).

We are indebted to Dr J. Leško, Department of Mass Spectrometry, Slovak Institute of Technology, Bratislava, for measurement of the mass spectra.

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Translated by M. Tichy.