*Russian Journal of General Chemistry, Vol. 72, No. 11, 2002, pp. 1714–1723. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 11, 2002, pp. 1818–1827.*


Dedicated to the centenary of Academician A.V. Kirsanov's birthday

# Synthesis of New 5-Mercapto-1,3-oxazole Derivatives on the Basis of 2-Acylamino-3,3-dichloroacrylonitriles and Their Analogs

**S. G. Pil'o, V. S. Brovarets, T. K. Vinogradova, A. V. Golovchenko, and B. S. Drach**

*Institute of Bioorganic and Petroleum Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine*

Received August 27, 2001

**Abstract** — Enamides of the general formula $Cl_2C{=}C(X)NHCOR^1$, where X = CN, COOAlk, $CONH_2$, $P(O)(OEt)_2$, $P(O)Ph_2$, $PPh_3^+ Cl^-$, were treated in succession with alkane- or arenethiols and silver carbonate to obtain 5-alkyl(aryl)thio-2-$R^1$-4-X-1,3-oxazoles with high selectivity. The latter were converted into the corresponding sulfonyl derivatives. Unlike 2-acylamino-3,3-dichloroacrylonitriles which react with sodium hydrogen sulfide in a nonselective fashion, reactions of derivatives like $Cl(ArS)C{=}C(CN)NHCOR^1$ with NaHS lead to hitherto unknown 5-arylthio-4-thiocarbamoyl-2-$R^1$-1,3-oxazoles whose structure was confirmed both by spectral methods and by cyclocondensation with bromoacetophenone according to Hantzsch. Heating of some 2-aryl-5-mercapto-4-X-1,3-oxazoles with benzenethiols results in recyclization into the corresponding 2,4-disubstituted 5-arylthio-1,3-thiazoles, presumably due to prototropic tautomerism in the 5-mercapto-oxazole fragment.

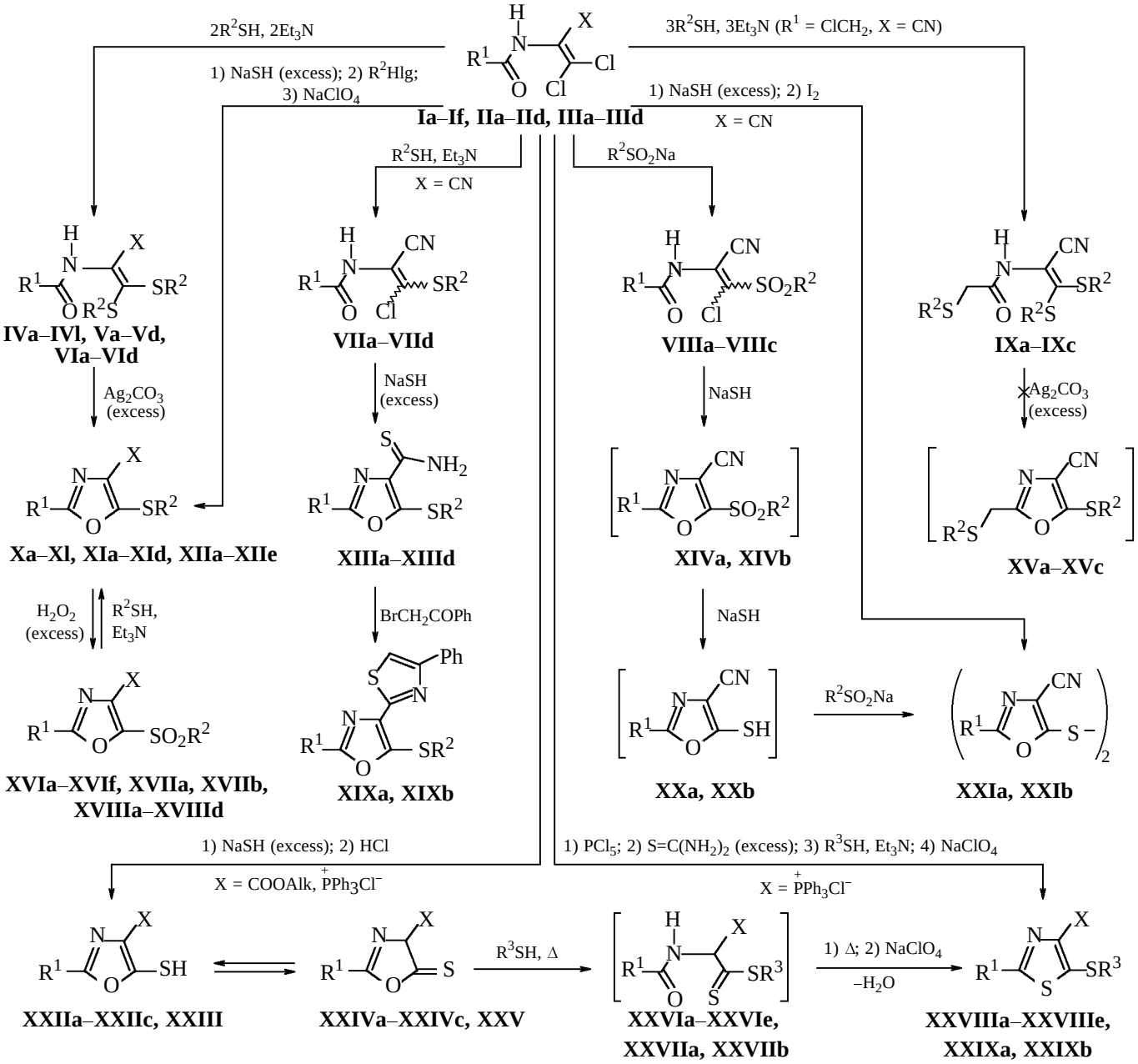
Reactions of accessible 2-acylamino-3,3-dichloroacrylonitriles **I** and structurally related enamides **II** and **III** with sulfur-centered nucleophiles were recently reviewed in [1] (which covers publications over the last three decades). As shown in [2–4], condensations of enamides **I**–**III** with aliphatic and aromatic thiols in the presence of triethylamine occur quite regioselectively. While performing the present work, we succeeded in considerably extending the scope of the known transformations **I** → **IV**, **II** → **V**, **III** → **VI**, and **I** → **VII** (Scheme 1), as well as effecting the condensations **I** → **VIII** and **I** → **IX** for the first time. As a result, we obtained six series of sulfur-containing enamides which were brought into further transformations with the goal of synthesizing 5-mercaptooxazole derivatives **X**–**XXI**. The most important were cyclocondensations of sulfur-containing enamides **IV**–**VI** with silver carbonate. Though the latter was proposed as a reagent for such cyclizations as early as 1976 [2], the limited and sometimes improper choice of sulfur-containing enamidonitriles made it impossible to estimate the preparative value of this approach in full measure.

We have found that cyclocondensations **IV** → **X**, **V** → **XI**, and **VI** → **XII** are particular cases of the general method for preparation of numerous 5-mercapto-1,3-oxazole derivatives containing various electron-acceptor substituents in position 4 of the oxazole ring, such as CN, C(O)OMe, C(O)OEt, $C(O)NH_2$, $P(O)(OEt)_2$, $P(O)Ph_2$, $PPh_3^+ ClO_4^-$, etc. Elimination of both aliphatic and aromatic thiols during the cyclization occurs almost equally readily. On the other hand, the rate of cyclocondensation is strongly affected by electron-acceptor power of the acyl residue in sulfur-containing enamides: aromatic acid derivatives undergo cyclization much more readily than do their aliphatic analogs. It was especially important to involve enamides **IV**–**VI** in the synthesis of 5-arylthio-4-X-1,3-oxazoles, for most of these were inaccessible previously. Apart from cyclocondensation of appropriate enamides **IV**–**VI** by the action of silver carbonate, alkylthio group can be introduced into position 5 of the oxazole ring via successive treatment of enamides **I**–**III** with sodium hydrogen sulfide and alkylating agents [4, 5]. The latter route is more convenient, e.g., for preparation of substituted 5-alkylthio-1,3-oxazoles having a triphenylphosphonium group in position 4 [4]; however, this procedure is almost unsuitable for the synthesis of 5-arylthio-1,3-oxazole derivatives.

Thus, the above two methods complement each other, so that they make it possible to synthesize numerous new 4-functionalized 5-alkylthio- and 5-arylthio-1,3-oxazoles **X**–**XII** which could be converted into sulfonyl derivatives **XVI**–**XVIII**. The latter are highly reactive toward nucleophiles. Treat-

1070-3632/02/7211-1714 $27.00 

**Scheme 1.**




**I**, X = NC (**a**–**f**); $R^1$ = $C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**), $CH_3$ (**c**), $ClCH_2$ (**d**), $(CH_3)_3C$ (**e**), H (**f**). **II**, X = $CH_3OCO$ (**a**, **b**); $R^1$ = $C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**); X = $C_2H_5OCO$, $R^1$ = $C_6H_5$ (**c**); X = $H_2NCO$, $R^1$ = $C_6H_5$ (**d**). **III**, X = $(C_2H_5O)_2PO$, $R^1$ = $C_6H_5$ (**a**); X = $(C_6H_5)_2PO$, $R^1$ = $C_6H_5$ (**b**); X = $(C_6H_5)_3P^+Cl^-$ (**c**, **d**); $R^1$ = $C_6H_5$ (**c**), 4-$CH_3C_6H_4$ (**d**). **IV**, X = NC (**a**–**l**); $R^1$ = $C_6H_5$, $R^2$ = $C_6H_5$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = $C_2H_5$ (**b**); $R^1$ = $C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**c**); $R^1$ = $R^2$ = 4-$CH_3C_6H_4$ (**d**); $R^1$ = $CH_3$, $R^2$ = 4-$CH_3C_6H_4$ (**e**); $R^1$ = $(CH_3)_3C$, $R^2$ = 4-$CH_3C_6H_4$ (**f**); $R^1$ = H, $R^2$ = 4-$CH_3C_6H_4$ (**g**); $R^1$ = $C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**h**); $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = 4-$ClC_6H_4$ (**i**); $R^1$ = $CH_3$, $R^2$ = 4-$ClC_6H_4$ (**j**); $R^1$ = $(CH_3)_3C$, $R^2$ = 4-$ClC_6H_4$ (**k**); $R^1$ = H, $R^2$ = 4-$ClC_6H_4$ (**l**). **V**, X = $CH_3OCO$ (**a**, **b**); $R^1$ = $C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = 4-$ClC_6H_4$ (**b**); X = $C_2H_5OCO$, $R^1$ = $C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**c**); X = $H_2NCO$, $R^1$ = $C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**d**). **VI**, X = $(C_2H_5O)_2P(O)$, $R^1$ = $C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**a**); X = $(C_6H_5)_2P(O)$, $R^1$ = $C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**b**); X = $(C_6H_5)_3P^+Cl^-$ (**c**, **d**); $R^1$ = $C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**c**); $R^1$ = $C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**d**). **VII**, X = NC (**a**–**d**); $R^1$ = $R^2$ = $C_6H_5$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = $C_6H_5$ (**b**); $R^1$ = $C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**c**); $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = 4-$ClC_6H_4$ (**d**). **VIII**, X = NC, $R^2$ = $C_6H_5$ (**a**–**c**); $R^1$ = $C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**), $CH_3$ (**c**). **IX**, $R^2$ = $C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**), 4-$ClC_6H_4$ (**c**). **X**, X = NC (**a**–**l**); $R^1$ = $C_6H_5$ (**a**),

4-$CH_3C_6H_4$ (**b**); $R^2 = C_2H_5$ (**a**, **b**); $R^1 = C_6H_5$ (**c**), 4-$CH_3C_6H_4$ (**d**), $CH_3$ (**e**), $(CH_3)_3C$ (**f**), H (**g**); $R^2$ = 4-$CH_3C_6H_4$ (**c**–**g**); $R^1 = C_6H_5$ (**h**), 4-$CH_3C_6H_4$ (**i**), $CH_3$ (**j**), $(CH_3)_3C$ (**k**), H (**l**); $R^2$ = 4-$ClC_6H_4$ (**h**–**l**). **XI**, X = $CH_3OCO$, $R^1 = C_6H_5$ (**a**); X = $CH_3OCO$, $R^1$ = 4-$CH_3C_6H_4$ (**b**); X = $C_2H_5OCO$, $R^1 = C_6H_5$ (**c**); X = $H_2NCO$, $R^1 = C_6H_5$ (**d**); $R^2$ = 4-$ClC_6H_4$ (**a**–**d**). **XII**, $R^1 = C_6H_5$ (**a**–**e**); X = $(C_2H_5O)_2P(O)$, $R^2$ = 4-$ClC_6H_4$ (**a**); X = $(C_6H_5)_2PO$, $R^2$ = 4-$CH_3C_6H_4$ (**b**); X = $(C_6H_5)_3P^+ClO_4^-$ (**c**–**e**); $R^2$ = 4-$ClC_6H_4$ (**c**), 4-$CH_3C_6H_4$ (**d**), $CH_3$ (**e**). **XIII**, X = $H_2NC(S)$ (**a**–**d**); $R^1 = R^2 = C_6H_5$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^2 = C_6H_5$ (**b**); $R^1 = C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**c**); $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = 4-$ClC_6H_4$ (**d**). **XIV**, $R^1 = R^2 = C_6H_5$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^2 = C_6H_5$ (**b**). **XV**, $R^2 = C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**), 4-$ClC_6H_4$ (**c**). **XVI**, X = NC (**a**–**f**); $R^1$ = 4-$CH_3C_6H_4$, $R^2 = C_2H_5$ (**a**); $R^1 = C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**b**); $R^1 = R^2$ = 4-$CH_3C_6H_4$ (**c**); $R^1 = C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**d**); $R^1$ = 4-$CH_3 \cdot C_6H_4$, $R^2$ = 4-$ClC_6H_4$ (**e**); $R^1 = CH_3$, $R^2$ = 4-$ClC_6H_4$ (**f**). **XVII**, X = $CH_3OCO$, $R^1$ = 4-$CH_3C_6H_4$, $R^2$ = 4-$ClC_6H_4$ (**a**); X = $C_2H_5OCO$, $R^1 = C_6H_5$, $R^2$ = 4-$ClC_6H_4$ (**b**). **XVIII**, $R^1 = C_6H_5$ (**a**–**d**); X = $(C_2H_5O)_2P(O)$, $R^2$ = 4-$ClC_6H_4$ (**a**); X = $(C_6H_5)_2 \cdot P(O)$, $R^2$ = 4-$CH_3C_6H_4$ (**b**); X = $(C_6H_5)_3P^+ClO_4^-$, $R^2 = CH_3$ (**c**); X = $(C_6H_5)_3P^+ClO_4^-$, $R^2$ = 4-$CH_3C_6H_4$ (**d**). **XIX**, $R^1 = C_6H_5$, $R^2$ = 4-$CH_3C_6H_4$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^2 = C_6H_5$ (**b**). **XX**, **XXI**, $R^1 = C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**). **XXII**, **XXIV**, X = $CH_3OCO$, $R^1 = C_6H_5$ (**a**); X = $CH_3OCO$, $R^1$ = 4-$CH_3C_6H_4$ (**b**); X = $C_2H_5OCO$, $R^1 = C_6H_5$ (**c**). **XXIII**, **XXV**, X = $(C_6H_5)_3P^+Cl^-$, $R^1 = C_6H_5$. **XXVI**, **XXVIII**, X = $CH_3OCO$ (**a**–**d**); $R^1 = C_6H_5$, $R^3$ = 4-$ClC_6H_4$ (**a**); $R^1$ = 4-$CH_3C_6H_4$, $R^3$ = 4-$ClC_6H_4$ (**b**); $R^1 = C_6H_5$, $R^3$ = 4-methoxycarbonyl-2-phenyl-1,3-oxazol-5-yl (**c**); $R^1$ = 4-$CH_3C_6H_4$, $R^3$ = 4-methoxycarbonyl-2-*p*-tolyl-1,3-oxazol-5-yl (**d**); X = $C_2H_5OCO$, $R^1 = C_6H_5$, $R^3$ = 4-ethoxycarbonyl-2-phenyl-1,3-oxazol-5-yl (**e**). **XXVII**, X = $(C_6H_5)_3P^+Cl^-$, $R^1 = C_6H_5$ (**a**, **b**); $R^3$ = 4-$CH_3C_6H_4$ (**a**), 4-$ClC_6H_4$ (**b**). **XXIX**, X = $(C_6H_5)_3P^+ClO_4^-$, $R^1 = C_6H_5$ (**a**, **b**); $R^3$ = 4-$CH_3C_6H_4$ (**a**), 4-$ClC_6H_4$ (**b**).

ment of **XVI**–**XVIII** with arenethiols in the presence of triethylamine under mild conditions leads to replacement of the sulfonyl moiety in position 5 of the oxazole ring by arylthio group due to effect of strong electron-acceptor substituent at the neighboring $C^4$ atom (see transformations **XVI** → **X**, **XVII** → **X**, and **XVIII** → **XII** in Scheme 1). Obviously, at least several of the transformations shown are important from the preparative viewpoint. However, additional studies are necessary to determine the scope and limits of application of reagents **XVI**–**XVIII** in the synthesis of new 5-functionalized 1,3-oxazoles.

Unlike enamidonitriles **I** whose reactions with sodium hydrogen sulfide take several pathways, their accessible derivatives **VII** react with NaHS in a more regioselective fashion, yielding previously unknown 5-arylthio-4-thiocarbamoyl-2-$R^1$-1,3-oxazoles **XIII**. The transformation of the cyano group into thiocarbamoyl was confirmed by the IR spectra and was reliably proved by the Hantzsch reaction of **XIII** with bromoacetophenone (**XIII** → **XIX**). In is interesting that structurally related enamidonitriles **VII** and **VIII** differently react with sodium hydrogen sulfide under the same conditions (DMF, 20–25°C). The cyano group in **VII** is involved in the reaction, whereas the cyano group in **VIII** remains intact; in the latter case, the major products are bis(2-aryl-4-cyano-1,3-oxazol-5-yl) disulfides **XXI**. Their structure is consistent with the IR and mass spectral data. In addition, compound **XXIa** was synthesized by an independent method by treatment of 2-benzoylamino-3,3-dichloroacrylonitrile first with sodium hydrogen sulfide and then with iodine [5]. It is quite probable that intermediate products **XIV** and **XX** play an important role in the complex transformation **III** → **XXI**. The possibility for oxidation of intermediate 4-cyano-5-mercapto-1,3-oxazoles **XX** with benzenesulfinate ion is beyond question; it was confirmed by model experiment (see Experimental). From the preparative viewpoint, the transformation **VIII** → **XXI** is more convenient than **I** → **XXI**.

To conclude, it should be noted that 2,4-disubstituted 5-mercaptooxazoles **XXII** (X = COOAlk) and **XXIII** (X = $\overset{+}{P}Ph_3Cl^-$) react in a specific manner with arene- and hetarenethiols on heating in ethanol or acetic acid (see Scheme 1). Obviously, these reactions involve intermediate formation of products **XXIV**–**XXVII** which are then converted into 5-mercaptothiazole derivatives **XXVIII** and **XXIX**. The structure of the final recyclization products was proved by independent synthesis of some of them via reaction of 2-aryl-5-chloro-1,3-thiazol-4-yl(triphenyl)phosphonium salts with arenethiols [6]. The transformation **XXII** → → **XXVIII** is especially important from the preparative viewpoint, for it leads to previously inaccessible 5-mercapto-1,3-thiazole-4-carboxylic acid derivatives. In these syntheses, the key stage is recyclization which is likely to be favored by prototropic tautomerism in the 5-mercaptooxazole fragment, giving rise to nonaromatic structures **XXIV** and **XXV**. The latter may be regarded as thio analogs of saturated azlactones which are known to undergo cleavage by the action of many reagents possessing a labile hydrogen atom, thiols among them. The subsequent elimination of water in acid medium and the cyclization **XXVI** → **XXVIII** or **XXVII** → **XXIX** have some close analogies (cf. [7]). Probably, the scope of the new recyclization could be extended even

in the nearest future, which could lead to development of a general procedure for the synthesis of previously inaccessible 1,3-thiazoles with functional substituents in positions 4,5.

## EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer in KBr (Table 1). The $^1$H NMR spectra were obtained on a Varian VXR-300 instrument in $(CD_3)_2SO$ or $CDCl_3$ using TMS as internal reference (Table 1). The mass spectra were run on a Varian MAT-311A spectrometer (Table 1). The yields, constants, and elemental analyses of the newly synthesized compounds are given in Table 2.

**2-Acylamino-3,3-dichloroacrylonitriles Ia–Id** were reported previously [9–11]. 3,3-Dichloro-2-pi-

**Table 1.** Spectral parameters of compounds **IV**, **VII–XIII**, **XVI–XIX**, **XXI**, and **XXVIII**

| Comp. no. | IR spectrum (KBr), ν, $cm^{-1}$ | $^1$H NMR spectrum [$(CD_3)_2SO$],[a] δ, ppm |
|---|---|---|
| **IVa** | 1655 (C=O), 2225 (C≡N), 3360 (NH as.) | 1.18 t (3H, $CH_3$), 1.30 t (3H, $CH_3$), 2.96 m (4H, $2CH_2$), 7.70–8.00 m (5H, $C_6H_5$), 10.17 s (1H, NH) |
| **IVb** | 1640 (C=O), 2220 (C≡N), 3300 (NH as.) | 1.17 t (3H, $CH_3$), 1.29 t (3H, $CH_3$), 2.38 s (3H, $CH_3C_6H_4$), 2.95 m (4H, $2CH_2$), 7.35 d (2H arom.), 7.82 (2H arom.), 10.14 s (1H, NH) |
| **IVc** | 1650 (C=O), 2215 (C≡N), 3220–3280 (NH as.) | 2.23 s (3H, $CH_3C_6H_4$), 2.32 s (3H, $CH_3C_6H_4$), 7.00–7.90 m (13H, $2C_6H_4$, $C_6H_5$), 10.35 s (1H, NH) |
| **IVd** | 1635 (C=O), 2220 (C≡N), 3260 (NH as.) | 2.23 s (3H, $CH_3C_6H_4S$), 2.31 s (3H, $CH_3C_6H_4S$), 2.37 s (3H, $CH_3C_6H_4CO$), 6.50–7.25 m (12H, $3C_6H_4$), 10.22 br.s (1H, NH) |
| **IVe** | – | 1.91 s (3H, $CH_3$), 2.30 s (6H, $2CH_3C_6H_4$), 7.00–7.20 m (8H, $2C_6H_4$), 9.97 s (1H, NH) |
| **IVf** | 1660 (C=O), 2220 (C≡N), 3270 (NH as.) | 1.15 s [9H, $(CH_3)_3C$], 2.32 s (3H, $CH_3C_6H_4$), 6.95–7.15 m (8H, $2C_6H_4$), 9.29 br.s (1H, NH) |
| **IVg** | – | 2.32 s (6H, $2CH_3$), 7.00–7.25 m (8H, $2C_6H_4$), 10.18 br.s (1H, NH) |
| **IVj** | 1690 (C–O), 2230 (C≡N), 3320 (NH as.) | 1.98 s (3H, $CH_3$), 7.10–7.50 m (8H, $2C_6H_4$), 9.98 br.s (1H, NH) |
| **IVk** | – | 1.17 s [9H, $(CH_3)C$], 7.10–7.40 m (8H, $2C_6H_4$), 9.51 s (1H, NH) |
| **IVl** | – | 7.10–7.50 m (8H, $2C_6H_4$), 10.34 s (1H, NH) |
| **VIIa**[b] | 1655 (C=O),[c] 2235 (C≡N),[c] 3250–3280 (NH as.) | 7.40–8.00 m (10H, $2C_6H_5$), 10.57 s (0.6H, NH), 10.63 s (0.4H, NH) |
| **VIIb**[b] | 1650 (C=O),[c] 2230 (C≡N),[c] 3230–3280 (NH as.) | 2.39 s (3H, $CH_3$), 7.20–7.90 m (9H, $C_6H_4$, $C_6H_5$), 10.46 s (0.7H, NH), 10.52 (0.3H, NH) |
| **VIIc**[b] | 1655 (C=O),[c] 2230 (C≡N),[c] 3260 (NH as.) | 2.35 s (2.1H, $CH_3$), 2.36 s (0.7H, $CH_3$), 7.00–8.00 m (9H, $C_6H_4$, $C_6H_5$), 10.53 s (0.7H, NH), 10.61 s (0.3H, NH) |
| **VIIIa** | 1715 (C=O), 2240 (C≡N), 3340 (NH as.) | – |
| **VIIIb**[b] | – | 2.38 s (2.1H, $CH_3$), 2.44 (0.9H, $CH_3$), 7.30–8.10 m (9H, $C_6H_4$, $C_6H_5$), 10.78 s (0.7H, NH), 10.82 s (0.3H, NH) |
| **VIIIc**[b] | – | 2.06 s (0.9H, $CH_3$), 2.12 (2.1H, $CH_3$), 7.60–8.10 m (5H, $C_6H_5$), 10.47 s (0.7H, NH), 10.53 s (0.3H, NH) |
| **IXa** | 1660 (C=O), 2225 (C≡N), 3220 (NH as.) | 3.80 s (2H, $CH_2$), 7.00–7.50 m (15H, $3C_6H_5$), 10.23 s (1H, NH) |
| **IXb** | 1655 (C=O), 2225 (C≡N), 3270 (NH as.) | 2.25 s (3H, $CH_3C_6H_4SCH_2$), 2.32 s (6H, $2CH_3C_6H_4$), 3.63 s (2H, $CH_2$), 6.90–7.40 m (12H, $3C_6H_4$), 10.04 s (1H, NH) |
| **IXc** | 1660 (C=O), 2230 (C≡N), 3260 (NH as.) | 3.77 s (2H, $CH_2$), 7.10–7.40 m (12H, $3C_6H_4$), 10.29 s (1H, NH) |
| **Xa** | 2260 (C≡N) | 1.39 t (3H, $CH_3$), 3.18 q (2H, $CH_2$), 7.50–8.10 m (5H, $C_6H_5$) |
| **Xb** | 2260 (C≡N) | 1.38 t (3H, $CH_3$), 2.42 s (3H, $CH_3$), 3.14 q (2H, $CH_2$), 7.37 d (2H arom.), 7.86 d (2H arom.) |
| **Xc** | 2260 (C≡N) | 2.32 s (3H, $CH_3$), 7.15–7.95 m (9H, $C_6H_5$, $C_6H_4$) |
| **Xd** | 2260 (C≡N) | 2.31 s (3H, $CH_3$), 2.38 s (3H, $CH_3$), 7.22–7.84 m (8H, $2C_6H_4$) |
| **Xe** | 2250 (C≡N) | 2.36 s (3H, $CH_3$), 2.46 s (3H, $CH_3C_6H_4$), 7.20 d (2H arom.), 7.40 d (2H arom.) |

**Table 1.** (Contd.)

| Comp. no. | IR spectrum (KBr), ν, $cm^{-1}$ | $^1H$ NMR spectrum [$(CD_3)_2SO$],[a] δ, ppm |
|---|---|---|
| **Xf** | 2255 (C≡N) | 1.26 s (9H, $3CH_3$), 2.33 s (3H, $CH_3$), 7.25 d (2H arom.), 7.34 d (2H arom.) |
| **Xg** | 2220 (C≡N) | 2.32 s (3H, $CH_3$), 6.90–7.20 m (5H, $C_6H_4$, CH) |
| **Xh** | 2255 (C≡N) | 7.43–8.05 m (9H, $C_6H_5$, $C_6H_4$) |
| **Xi** | 2260 (C≡N) | 2.39 s (3H, $CH_3$), 7.40 d (2H arom.), 7.52 d (2H arom), 7.60 d (2H arom.), 7.86 d (2H arom.) |
| **Xj** | 2250 (C≡N) | 2.49 s (3H, $CH_3$), 7.37 d (2H arom.), 7.43 d (2H arom.) |
| **Xk** | 2250 (C≡N) | 1.33 s (9H, $3CH_3$), 7.46 s (4H, $C_6H_4$) |
| **Xl** | 2225 (C≡N) | 7.15–7.32 m (5H, $C_6H_4$, CH) |
| **XIa** | – | 3.90 s (3H, $OCH_3$), 7.42–7.80 m (9H, $C_6H_5$, $C_6H_4$) |
| **XIb** | 1700 (C=O) | 2.35 s (3H, $CH_3$), 3.85 s (3H, $OCH_3$), 7.24–7.80 m (8H, $2C_6H_4$) |
| **XIc** | – | 1.31 t (3H, $CH_3$), 4.32 q (2H, $CH_2$), 7.45–7.85 m (9H, $C_6H_5$, $C_6H_4$) |
| **XId** | – | 7.43–7.88 m (11H, $C_6H_5$, $C_6H_4$, $NH_2$) |
| **XIIa** | 1270 (P=O) | 1.27 t (6H, $2CH_3$), 4.14 q (4H, $2CH_2$), 7.42–7.94 m (9H, $C_6H_5$, $C_6H_4$) |
| **XIIb** | 1190 (P=O) | 2.28 s (3H, $CH_3$), 7.17–7.92 m (19H, $3C_6H_5$, $C_6H_4$) |
| **XIId** | – | 2.34 s (3H, $CH_3$), 7.21–7.98 m (24H, $4C_6H_5$, $C_6H_4$) |
| **XIIIa** | 1635 [δ($NH_2$)], 3100–3600 (NH as.) | 7.30–7.95 m (10H, $2C_6H_5$), 9.43 s (2H, $NH_2$) |
| **XIIIb** | 1635 [δ($NH_2$)], 3300–3500 (NH as.) | 2.38 s (3H, $CH_3$), 7.30–7.90 m (9H, $C_6H_5$, $C_6H_4$), 9.41 s (2H, $NH_2$) |
| **XIIIc** | 1635 [δ($NH_2$)], 3300–3500 (NH as.) | 2.38 s (3H, $CH_3$), 7.31–7.92 m (9H, $C_6H_5$, $C_6H_4$), 9.41 s (2H, $NH_2$) |
| **XIIId** | – | 2.40 s (3H, $CH_3$), 7.32–8.05 m (8H, $2C_6H_4$), 9.36 s (2H, $NH_2$) |
| **XVIa** | 2260 (C≡N) | 1.34 t (3H, $CH_3CH_2$), 2.44 s (3H, $CH_3C_6H_4$), 3.63 q (2H, $CH_2$), 7.44 d (2H arom.), 7.96 d (2H arom.) |
| **XVIb** | 2260 (C≡N) | 2.44 s (3H, $CH_3$), 7.55–8.10 m (9H, $C_6H_4$, $C_6H_5$) |
| **XVIc** | 2260 (C≡N) | 2.40 s (3H, $CH_3$), 2.44 s (3H, $CH_3$), 7.35–8.05 m (8H, $2C_6H_4$) |
| **XVId** | 2260 (C≡N) | 7.55–8.20 m (9H, $C_6H_4$, $C_6H_5$) |
| **XVIe**[d] | 2250 (C≡N) | 2.40 s (3H, $CH_3$), 7.35–8.20 m (8H, $2C_6H_4$) |
| **XVIf** | – | 2.56 s (3H, $CH_3$), 7.63 d (2H arom.), 8.01 d (2H arom.) |
| **XVIIb** | – | 1.37 t (3H, $CH_3$), 4.40 q (2H, $CH_2$), 7.55–8.20 m (9H, $C_6H_5$, $C_6H_4$) |
| **XVIIIa** | – | 1.37 t (6H, $2CH_3$), 4.25 q (4H, $2CH_2$), 7.50–8.20 m (9H, $C_6H_5$, $C_6H_4$) |
| **XIXa** | – | 2.27 s (3H, $CH_3$), 7.10–8.10 m (15H, $2C_6H_5$, $C_6H_4$, CH) |
| **XIXb** | – | 2.43 s (3H, $CH_3$), 7.09–8.09 m (15H, $2C_6H_5$, $C_6H_4$, CH) |
| **XXIa**[e] | 2255 (C≡N) | 7.60–8.03 m (10H, $2C_6H_5$) |
| **XXIb**[f] | 2260 (C≡N) | 2.40 s (6H, $2CH_3$), 7.38 d (4H arom.), 7.87 d (4H arom.) |
| **XXVIIIa** | 1700 (C=O) | 3.90 s (3H, $OCH_3$), 7.40–7.80 m (9H, $C_6H_5$, $C_6H_4$) |
| **XXVIIIb** | – | 2.33 s (3H, $CH_3$), 3.90 s (3H, $OCH_3$), 7.22–7.80 m (8H, $2C_6H_4$) |
| **XXVIIIc** | 1690 (C=O) | 3.99 s (3H, $OCH_3$), 4.04 s (3H, $OCH_3$), 7.84–8.10 m (10H, $2C_6H_5$) |
| **XXVIIId** | 1700 (C=O) | 2.40 s (3H, $CH_3$), 2.44 s (3H, $CH_3$), 4.00 s (3H, $OCH_3$), 4.00 s (3H, $OCH_3$) |
| **XXVIIIe** | 1680 (C=O) | 1.40 t (6H, $2CH_3$), 4.48 q (4H, $2CH_2$), 7.44–8.10 m (10H, $2C_6H_5$) |

[a] The $^1H$ NMR spectra of **Xe**, **Xj**, and **XVIf** were recorded in $CDCl_3$. [b] Data for a mixture of *Z* and **E** isomers. [c] Band with a shoulder. [d] Mass spectrum, *m*/*z*: 358 [$M^+$], 199, 183, 155, 144, 119, 111, 103, 89, 77, 63. [e] Mass spectrum, *m*/*z*: 402 [$M^+$], 368, 341, 326, 310, 279, 265, 255, 236, 213, 202, 185, 169, 157, 149, 141, 121, 105, 95, 81, 69. [f] Mass spectrum, *m*/*z*: 430 [$M^+$], 216, 188, 183, 155, 135, 119, 103, 91, 77, 65.

valoylaminoacrylonitrile (**Ie**) and 3,3-dichloro-2-formylacrylonitrile (**If**) were synthesized by the procedure described in [9] for compound **Ic**, by reactions of the corresponding *N*-1,2,2,2-tetrachloroethylamides with aqueous sodium cyanide. Alkyl 2-acylamino-3,3-dichloroacrylates **IIa**–**IIc** [12], 2-benzoylamino-3,3-dichloroacrylamide (**IId**) [12], and phosphorus-containing enamides **IIIa**–**IIId** [13, 14] were synthesized by known methods.

**Table 2.** Yields, constants, and elemental analyses of compounds **I**, **IV**–**XIII**, **XVI**–**XIX**, **XXI**, **XXVIII**, and **XXIX**

| Comp. no. | Yield, % | mp, °C (solvent) | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cl | N | S (P) | | Cl | N | S (P) |
| **Ie** | 70 | 94–96 (benzene) | 32.12 | 12.60 | – | $C_8H_{10}Cl_2N_2O$ | 32.07 | 12.67 | – |
| **If**[a] | 65 | 147–149 (benzene) | 42.90 | 16.90 | – | $C_4H_2Cl_2N_2O$ | 42.98 | 16.98 | – |
| **IVa** | 75 | 96–98 (ethanol) | – | 9.50 | 21.95 | $C_{14}H_{16}N_2OS_2$ | – | 9.58 | 21.93 |
| **IVb** | 78 | 116–118 (ethanol) | – | 9.08 | 20.96 | $C_{15}H_{18}N_2OS_2$ | – | 9.14 | 20.93 |
| **IVc** | 76 | 162–164 (ethanol) | – | 6.68 | 15.40 | $C_{24}H_{20}N_2OS_2$ | – | 6.73 | 15.39 |
| **IVd** | 80 | 120–122 (ethanol) | – | 6.47 | 14.92 | $C_{25}H_{22}N_2OS_2$ | – | 6.51 | 14.89 |
| **IVe** | 70 | 144–146 (ethanol) | – | 7.85 | 18.10 | $C_{19}H_{18}N_2OS_2$ | – | 7.90 | 18.09 |
| **IVf** | 75 | 143–145 (ethanol) | – | 7.02 | 16.20 | $C_{22}H_{24}N_2OS_2$ | – | 7.06 | 16.17 |
| **IVg** | 60 | 118–120 (benzene) | – | 8.18 | 18.80 | $C_{18}H_{16}N_2OS_2$ | – | 8.23 | 18.84 |
| **IVi** | 85 | 135–137 (ethanol) | 15.05 | 5.90 | 13.56 | $C_{23}H_{16}Cl_2N_2OS_2$ | 15.03 | 5.94 | 13.60 |
| **IVj** | 80 | 180–182 (ethanol) | 17.90 | 7.05 | 16.20 | $C_{17}H_{12}Cl_2N_2OS_2$ | 17.95 | 7.09 | 16.22 |
| **IVk** | 75 | 123–125 (ethanol) | 16.10 | 6.35 | 14.60 | $C_{20}H_{18}Cl_2N_2OS_2$ | 16.21 | 6.40 | 14.66 |
| **IVl** | 85 | 185–187 (toluene) | 18.42 | 7.30 | 16.80 | $C_{16}H_{10}Cl_2N_2OS_2$ | 18.60 | 7.35 | 16.82 |
| **Va** | 70 | 62–65 (ethanol) | 14.40 | 2.82 | 13.01 | $C_{23}H_{17}Cl_2NO_3S_2$ | 14.45 | 2.86 | 13.08 |
| **Vb** | 75 | 73–75 (ethanol) | 13.90 | 2.75 | 12.65 | $C_{24}H_{19}Cl_2NO_3S_2$ | 14.06 | 2.78 | 12.71 |
| **Vc**[b] | 70 | – | 13.81 | 2.74 | 12.60 | $C_{24}H_{19}Cl_2NO_3S_2$ | 14.06 | 2.78 | 12.71 |
| **Vd** | 70 | 223–225 (ethanol) | 14.79 | 5.80 | 13.41 | $C_{22}H_{16}Cl_2N_2O_2S_2$ | 14.91 | 5.86 | 13.49 |
| **VIa** | 75 | 178–180 (benzene) | 12.40 | 2.42 | 11.25 | $C_{25}H_{24}Cl_2NO_4PS_2$ | 12.47 | 2.46 | 11.28 |
| **VIb** | 75 | 234–236 (benzene) | – | 2.33 | 10.80 (5.20) | $C_{35}H_{30}NO_2PS_2$ | – | 2.37 | 10.84 (5.23) |
| **VIIa** | 82 | 148–150 (ethanol) | 11.20 | 8.82 | 10.10 | $C_{16}H_{11}ClN_2OS$ | 11.26 | 8.90 | 10.19 |
| **VIIb** | 84 | 118–120 (ethanol) | 10.80 | 8.50 | 9.72 | $C_{17}H_{13}ClN_2OS$ | 10.78 | 8.52 | 9.75 |
| **VIIc** | 85 | 134–136 (ethanol) | 10.76 | 8.48 | 9.70 | $C_{17}H_{13}ClN_2OS$ | 10.78 | 8.52 | 9.75 |
| **VIId** | 84 | 155–157 (ethanol) | 19.45 | 7.70 | 8.80 | $C_{17}H_{12}Cl_2N_2OS$ | 19.52 | 7.71 | 8.83 |
| **VIIIa** | 70 | 165–167 (ethanol) | 10.11 | 8.05 | 9.20 | $C_{16}H_{11}ClN_2O_3S$ | 10.22 | 8.08 | 9.25 |
| **VIIIb** | 70 | 188–190 (ethanol) | 9.52 | 7.70 | 8.80 | $C_{17}H_{13}ClN_2O_3S$ | 9.83 | 7.76 | 8.89 |
| **VIIIc** | 75 | 115–117 (ethanol) | 12.40 | 9.80 | 11.20 | $C_{11}H_9ClN_2O_3S$ | 12.45 | 9.84 | 11.26 |
| **IXa** | 85 | 120–122 (ethanol) | – | 6.40 | 22.10 | $C_{23}H_{18}N_2OS_3$ | – | 6.45 | 22.13 |
| **IXb** | 85 | 128–130 (ethanol) | – | 5.80 | 20.20 | $C_{26}H_{24}N_2OS_3$ | – | 5.88 | 20.18 |
| **IXc** | 85 | 142–144 (ethanol) | 19.70 | 5.15 | 17.80 | $C_{23}H_{15}Cl_3N_2OS_3$ | 19.77 | 5.21 | 17.88 |
| **Xa**[c] | 62 | 58–60 (ethanol) | – | 12.10 | 13.90 | $C_{12}H_{10}N_2OS$ | – | 12.16 | 13.92 |
| **Xb**[d] | 65 | 82–84 (ethanol) | – | 11.40 | 13.10 | $C_{13}H_{12}N_2OS$ | – | 11.47 | 13.12 |
| **Xc**[e] | 76 | 78–80 (ethanol) | – | 9.50 | 10.92 | $C_{17}H_{12}N_2OS$ | – | 9.58 | 10.97 |
| **Xd** | 75 | 116–118 (ethanol) | – | 9.10 | 10.45 | $C_{18}H_{14}N_2OS$ | – | 9.14 | 10.47 |
| **Xe** | 52 | 52–54 (hexane) | – | 12.08 | 13.90 | $C_{12}H_{10}N_2OS$ | – | 12.16 | 13.92 |
| **Xf** | 50 | 74–76 (hexane) | – | 10.24 | 11.80 | $C_{15}H_{16}N_2OS$ | – | 10.29 | 11.77 |
| **Xg** | 50 | 176–178 (ethanol) | – | 12.88 | 14.80 | $C_{11}H_8N_2OS$ | – | 12.95 | 14.83 |
| **Xh** | 76 | 83–85 (ethanol) | 11.22 | 8.90 | 10.24 | $C_{16}H_9ClN_2OS$ | 11.34 | 8.96 | 10.25 |
| **Xi** | 75 | 104–106 (ethanol) | 10.80 | 8.50 | 9.76 | $C_{17}H_{11}ClN_2OS$ | 10.85 | 8.57 | 9.81 |
| **Xj** | 56 | 68–70 (ethanol) | 14.10 | 11.12 | 12.70 | $C_{11}H_7ClN_2OS$ | 14.14 | 11.17 | 12.79 |
| **Xk** | 58 | 65–67 (ethanol) | 12.05 | 9.50 | 10.90 | $C_{14}H_{13}ClN_2OS$ | 12.11 | 9.57 | 10.95 |
| **Xl** | 50 | 180–182 (benzene) | 14.90 | 11.80 | 13.56 | $C_{10}H_5ClN_2OS$ | 14.98 | 11.84 | 13.55 |
| **XIa** | 65 | 110–112 (ethanol) | 10.10 | 4.01 | 9.25 | $C_{17}H_{12}ClNO_3S$ | 10.25 | 4.04 | 9.27 |
| **XIb** | 65 | 120–122 (ethanol) | 9.80 | 3.85 | 8.90 | $C_{18}H_{14}ClNO_3S$ | 9.85 | 3.89 | 8.91 |
| **XIc** | 60 | 98–100 (ethanol) | 9.72 | 3.84 | 8.86 | $C_{18}H_{14}ClNO_3S$ | 9.85 | 3.89 | 8.91 |
| **XId** | 50 | 250–252 (ethanol) | 10.60 | 8.40 | 9.65 | $C_{16}H_{11}ClN_2O_2S$ | 10.72 | 8.47 | 9.69 |
| **XIIa** | 50 | 36–38 (hexane) | 8.25 | 3.30 | 7.50 (7.30) | $C_{19}H_{19}ClNO_4PS$ | 8.37 | 3.31 | 7.57 (7.31) |

**Table 2.** (Contd.)

| Comp. no. | Yield, % | mp, °C (solvent) | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cl | N | S (P) | | Cl | N | S (P) |
| **XIIb** | 60 | 153–155 (benzene) | – | 3.00 | 6.80 (6.60) | $C_{28}H_{22}NO_2PS$ | – | 3.00 | 6.86 (6.63) |
| **XIId** | 62 | 142–143 (methanol) | 5.85 | 2.35 | 5.40 (5.20) | $C_{34}H_{27}ClNO_5PS$ | 5.64 | 2.23 | 5.11 (4.93) |
| **XIIIa** | 50 | 192–194 (ethanol) | – | 8.90 | 20.50 | $C_{16}H_{12}N_2OS_2$ | – | 8.97 | 20.53 |
| **XIIIb** | 50 | 206–208 (ethanol) | – | 8.50 | 19.62 | $C_{17}H_{14}N_2OS_2$ | – | 8.58 | 19.65 |
| **XIIIc** | 52 | 215–217 (ethanol) | – | 8.53 | 19.60 | $C_{17}H_{14}N_2OS_2$ | – | 8.58 | 19.65 |
| **XIIId** | 52 | 194–196 (ethanol) | 9.84 | 7.72 | 17.78 | $C_{17}H_{13}ClN_2OS_2$ | 9.82 | 7.76 | 17.77 |
| **XVIa** | 50 | 147–149 (ethanol) | – | 10.10 | 11.63 | $C_{13}H_{12}N_2O_3S$ | – | 10.14 | 11.60 |
| **XVIb**[f] | 50 | 180–182 (acetic acid) | – | 8.60 | 9.85 | $C_{17}H_{12}N_2O_3S$ | – | 8.64 | 9.89 |
| **XVIc** | 54 | 200–202 (acetic acid) | – | 8.24 | 9.45 | $C_{18}H_{14}N_2O_3S$ | – | 8.28 | 9.48 |
| **XVId** | 60 | 176–178 (acetic acid) | 10.20 | 8.08 | 9.28 | $C_{16}H_9ClN_2O_3S$ | 10.28 | 8.13 | 9.30 |
| **XVIe** | 60 | 208–210 (acetic acid) | 9.85 | 7.80 | 8.90 | $C_{17}H_{11}ClN_2O_3S$ | 9.88 | 7.81 | 8.94 |
| **XVIf** | 50 | 130–132 (ethanol) | 12.50 | 9.86 | 11.30 | $C_{11}H_7ClN_2O_3S$ | 12.54 | 9.91 | 11.34 |
| **XVIIa** | 56 | 208–210 (acetic acid) | 9.10 | 3.48 | 8.12 | $C_{18}H_{14}ClNO_5S$ | 9.05 | 3.57 | 8.18 |
| **XVIIb** | 60 | 138–140 (acetic acid) | 9.12 | 3.46 | 8.20 | $C_{18}H_{14}ClNO_5S$ | 9.05 | 3.57 | 8.18 |
| **XVIIIa** | 60 | 107–109 (ethanol) | 7.70 | 3.05 | 7.05 (6.70) | $C_{19}H_{19}ClNO_6PS$ | 7.78 | 3.07 | 7.03 (6.79) |
| **XVIIIb** | 60 | >250 (ethanol) | – | 2.76 | 6.40 (6.05) | $C_{28}H_{22}NO_4PS$ | – | 2.80 | 6.42 (6.20) |
| **XVIIIc** | 70 | >250 (acetic acid) | 6.10 | 2.40 | 5.45 (5.35) | $C_{28}H_{23}ClNO_7PS$ | 6.07 | 2.40 | 5.49 (5.30) |
| **XVIIId** | 65 | 220–221 (methanol–water, 3 : 1) | 5.20 | 2.00 | 4.71 (4.40) | $C_{34}H_{27}ClNO_7PS$ | 5.37 | 2.12 | 4.86 (4.69) |
| **XIXa** | 50 | 190–192 (ethanol–water, 3 : 1) | – | 6.50 | 15.10 | $C_{25}H_{18}N_2OS_2$ | – | 6.57 | 15.03 |
| **XIXb**[g] | 54 | 195–197 (ethanol–water, 3 : 1) | – | 6.48 | 15.05 | $C_{25}H_{18}N_2OS_2$ | – | 6.57 | 15.03 |
| **XXIa** | 60 | 214–216 (dioxane) | – | 13.90 | 15.95 | $C_{20}H_{10}N_4O_2S_2$ | – | 13.92 | 15.93 |
| **XXIb** | 60 | 196–198 (dioxane) | – | 13.05 | 14.95 | $C_{22}H_{14}N_4O_2S_2$ | – | 13.01 | 14.90 |
| **XXVIIIa** | 62 | 108–110 (ethanol) | 9.84 | 3.80 | 17.70 | $C_{17}H_{12}ClNO_2S_2$ | 9.80 | 3.87 | 17.72 |
| **XXVIIIb** | 68 | 150–152 (ethanol) | 9.45 | 3.70 | 17.10 | $C_{18}H_{14}ClNO_2S_2$ | 9.43 | 3.73 | 17.06 |
| **XXVIIIc** | 70 | 164–165 (acetone) | – | 6.15 | 14.15 | $C_{22}H_{16}N_2O_5S_2$ | – | 6.19 | 14.17 |
| **XXVIIId** | 75 | 222–224 (nitro-methane) | – | 5.76 | 13.30 | $C_{24}H_{20}N_2O_5S_2$ | – | 5.82 | 13.34 |
| **XXVIIIe** | 72 | 140–142 (methanol) | – | 5.75 | 13.35 | $C_{24}H_{20}N_2O_5S_2$ | – | 5.82 | 13.34 |
| **XXIXa** | 70 | 232–234 (methanol) | 5.40 | 2.10 | 9.95 (4.85) | $C_{34}H_{27}ClNO_4PS_2$ | 5.50 | 2.17 | 9.96 (4.81) |
| **XXIXb** | 90 | 195–197 (methanol) | 10.60 | 2.10 | 9.70 (4.65) | $C_{33}H_{24}Cl_2NO_4PS_2$ | 10.67 | 2.11 | 9.65 (4.66) |

[a] Data for compound **If** prepared as described in [8], mp 148–150°C. [b] Thick oily substance which cannot be distilled under reduced pressure. It was brought into further syntheses without purification. [c] Found, %: C 62.30; H 4.59. Calculated, %: C 62.59; H 4.38. [d] Found, %: C 63.68; H 5.37. Calculated, %: C 63.91; H 4.95. [e] Found, %: C 69.53; H 4.43. Calculated, %: C 69.84; H 4.14. [f] Found, %: C 62.61; H 4.05. Calculated, %: C 62.95; H 3.73. [g] Found, %: C 70.17; H 4.62. Calculated, %: C 70.40; H 4.25.

**2-Acylamino-3,3-bis[alkylthio(arylthio)]acrylonitriles IVa–IVl.** To a solution of 0.01 mol of enamidonitrile **Ia**–**Ic** or **If** in 30 ml of anhydrous acetonitrile we added 0.02 mol of the corresponding thiol and 0.02 mol of triethylamine, the mixture was kept for 8 h at 20–25°C, the precipitate was filtered off, the filtrate was evaporated, and the residue was treated with water, dried, and purified by recrystallization.

**2-Benzoylamino-3,3-bis(*p*-chlorophenylthio)acrylonitrile (IVh)** was reported in [3].

**Alkyl 2-acylamino-3,3-bis(*p*-chlorophenylthio)acrylates Va–Vc and 2-benzoylamino-3,3-bis(*p*-chlorophenylthio)acrylamide (Vd)** were synthesized as described above for compounds **IVa**–**IVl**; the reaction mixture was kept for 48 h at 20–25°C.

**Diethyl 1-benzoylamino-2,2-bis(*p*-chlorophenylthio)ethenylphosphonate (VIa) and 1-benzoylamino-2,2-bis(*p*-tolylthio)ethenyl(diphenyl)phosphine oxide (VIa)** were synthesized as described above for compounds **IVa**–**IVl**.

**1-Benzoylamino-2,2-bis[*p*-chlorophenylthio-(*p*-tolylthio)]ethenyl(triphenyl)phosphonium chlorides VIc and VId** were synthesized as described previously [4].

**3-Arylthio-2-acylamino-3-chloroacrylonitriles VIIa–VIId.** To a solution of 0.01 mol of compound **Ia** or **Ib** in 30 ml of anhydrous acetonitrile we added 0.01 mol of the corresponding thiol and 0.01 mol of triethylamine. The mixture was kept for 8 h at 20–25°C, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the residue was treated with water, dried, and recrystallized from ethanol. Compounds **VIIa**–**VIId** were isolated as mixtures of *Z* and *E* isomers (Tables 1, 2).

**2-Acylamino-3-chloro-3-phenylsulfonyacrylonitriles VIIIa–VIIIc.** A suspension of 0.01 mol of compound **Ia**–**Ic** and 0.01 mol of anhydrous sodium benzenesulfinate in 50 ml of anhydrous acetonitrile was refluxed for 12 h. The mixture was then kept for 8 h at 20–25°C, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the residue was treated with water, dried, and purified by recrystallization.

**2-Arylthioacetylamino-3,3-bis(arylthio)acrylonitriles IXa–IXc.** To a solution of 0.01 mol of compound **Id** [11] in 40 ml of anhydrous acetonitrile we added 0.03 mol of the corresponding thiol and 0.03 mol of triethylamine, and the mixture was kept for 8 h at 20–25°C. The precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the residue was treated with water, dried, and purified by recrystallization.

**5-Alkyl(aryl)thio-2-aryl-4-cyano-1,3-oxazoles Xa–Xd, Xh, and Xi.** *a*. A suspension of 0.01 mol of compound **IVa**–**IVd**, **IVh**, or **IVi** and 0.03 mol of freshly prepared silver carbonate in 40 ml of anhydrous acetonitrile was refluxed for 8–10 h, the mixture was left to stand for 8 h at 20–25°C, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, the residue was treated with water, and the precipitate was filtered off, dried, and purified by recrystallization.

*b*. To a solution of 0.005 mol of compound **XVIe** (see below) and 10 ml of dioxane we added 0.0075 mol of *p*-toluenethiol and 0.0075 mol of triethylamine. The mixture was refluxed for 8 h, kept for 24 h at 20–25°C, and evaporated under reduced pressure. The residue was washed with water, dried, and purified by crystallization. Yield of **Xd** 70%. Samples of **Xd** prepared as described in *a* and *b* showed no depression of the melting point on mixing.

**2-Alkyl-5-arylthio-4-cyano-1,3-oxazoles Xe, Xf, Xj, and Xk.** A suspension of 0.01 mol of compound **IVe**, **IVf**, **IVj**, and **IVk** and 0.03 mol of silver carbonate in 40 ml of anhydrous dioxane was refluxed for 25 h. The mixture was then kept for 8 h at 20–25°C, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, the residue was treated with water, and the precipitate was filtered off, dried, and purified by recrystallization.

**5-Arylthio-4-cyano-1,3-oxazoles Xg and Xl** were synthesized similarly.

**Alkyl 2-aryl-5-*p*-chlorophenylthio-1,3-oxazole-4-carboxylates XIa–XIc** were synthesized as described above for compounds **Xa**–**Xd**.

**2-Aryl-5-arylthio-1,3-oxazol-4-yl(triphenyl)phosphonium perchlorates XIIc and XIId.** *a*. To a solution of 0.01 mol of phosphonium salt **VIc** or **VId** in acetonitrile we added 0.004 mol of freshly prepared silver carbonate, and the resulting suspension was refluxed for 18–20 h under stirring. The precipitate was filtered off, the most part of the solvent was removed under reduced pressure, 2 ml of a saturated aqueous solution of sodium perchlorate was added to the residue, and the precipitate was filtered off, washed with water, and recrystallized from methanol.

*b*. To a suspension of 0.001 mol of compound **XVIIIc** (see below) in 20 ml of anhydrous acetonitrile we added 0.001 mol of *p*-toluenethiol and 0.0012 mol of triethylamine. The mixture was heated at 60°C until it became homogeneous (3 h), the solvent was removed under reduced pressure, 3 ml of methanol and 2 ml of a saturated aqueous solution of sodium perchlorate was added, the mixture was kept for 24 h,

and the precipitate was filtered off and purified by recrystallization from methanol. Yield of **XIId** 65%. The $^1$H and IR spectra of two samples of **XIId** prepared as described in *a* and *b* were identical.

**5-Methylthio-2-phenyl-1,3-oxazol-4-yl(triphenyl)-phosphonium perchlorate (XIIe)** was obtained by treatment of 5-methylthio-2-phenyl-1,3-oxazol-4-yl-(triphenyl)phosphonium iodide [4] with an aqueous solution of sodium perchlorate.

**2-Aryl-5-arylthio-4-thiocarbamoyl-1,3-oxazoles XIIIa–XIIId.** To a solution of 0.005 mol of compound **VIIa–VIId** in 10 ml of dimethylformamide we added 0.015 mol of freshly prepared sodium hydrogen sulfide, the mixture was kept for 48 h at 20–25°C, the precipitate was filtered off, the solvent was removed from the filtrate under reduced pressure, the oily residue was treated with 5% hydrochloric acid, and the precipitate was filtered off and purified by recrystallization.

**2-Alkyl(aryl)-5-arylsulfonyl-1,3-oxazoles XVIa–XVIf, XVIIa, XVIIb, and XVIIIa–XVIIId.** A solution of 0.005 mol of compound **Xb–Xd**, **Xh–Xj**, **XIa**, **XIb**, **XIIa**, **XIIb**, **XIId**, or **XIIe** in 10 ml of glacial acetic acid was heated to the boiling point, and three 1-ml portions of 30% hydrogen peroxide were added through equal time intervals over a period of 2 h. The mixture was kept for 8 h at 20–25°C, and the precipitate was filtered off and purified by recrystallization.

**2-Aryl-5-arylthio-4-(4-phenyl-1,3-thiazol-2-yl)-1,3-oxazoles XIXa and XIXb.** To a solution of 0.005 mol of compound **XIIIb** or **XIIIc** in 15 ml of ethanol we added 0.006 mol of bromoacetophenone, and the mixture was refluxed for 2 h and kept for 8 h at 20–25°C. It was then evaporated by half in a vacuum, the residue was treated with a saturated solution of sodium hydrogen carbonate until alkaline reaction, the mixture was heated for 10–15 min to 50–60°C and kept for 8 h at 20–25°C, and the precipitate was filtered off and purified by recrystallization.

**Bis(2-aryl-4-cyano-1,3-oxazol-5-yl) disulfides XXIa and XXIb.** *a*. To a solution of 0.005 mol of compound **VIIIa** or **VIIIb** in 10 ml of dimethylformamide we added 0.015 mol of sodium hydrogen sulfide, the mixture was kept for 48 h at 20–25°C, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, the residue was treated with water, and the precipitate was filtered off, dried, and purified by recrystallization.

*b*. Compound **XXIa** was synthesized previously by oxidation of crude 4-cyano-5-mercapto-2-phenyl-1,3-oxazole with iodine [5]. No depression of the melting point was observed on mixing samples of **XXIa** prepared as described in *a* and *b*.

**Methyl 2-aryl-4-*p*-chlorophenylthio-1,3-thiazole-4-carboxylates XXVIIIa and XXVIIIb.** To a solution of 0.005 mol of compound **XXIIa** or **XXIIb** [5] in 30 ml of ethanol we added 0.025 mol of *p*-chlorobenzenethiol. The mixture was refluxed for 8 h and was then kept for 8 h at 20–25°C, and the precipitate was filtered off, washed with a saturated solution of sodium hydrogen carbonate, and purified by recrystallization.

**4-Alkoxycarbonyl-2-aryl-1,3-oxazol-5-yl 4-alkoxycarbonyl-2-aryl-1,3-thiazol-5-yl sulfides XXVIIIc–XXVIIIe.** A suspension of 0.005 mol of compound **XXIIa–XXIIc** [5] in 20 ml of methanol or ethanol was refluxed for 30–40 min. The mixture was cooled, and the precipitate was filtered off and purified by recrystallization.

**5-Arylthio-2-phenyl-1,3-thiazol-4-yl(triphenyl)-phosphonium perchlorates XXIXa and XXIXb.** *a*. To a solution of 0.001 mol of 2-phenyl-4-triphenylphosphonio-1,3-oxazole-5-thiolate [4] in 10 ml of glacial acetic acid we added 0.01 mol of the corresponding thiol. The mixture was heated to the boiling point and saturated with hydrogen chloride over a period of 2 h, 2 ml of a saturated aqueous solution of sodium perchlorate was added, the mixture was kept for 24 h at 20–25°C, and the precipitate was filtered off and purified by recrystallization.

*b*. Compound **XXIXb** was also synthesized by reaction of *p*-chlorobenzenethiol with 5-chloro-2-phenyl-1,3-thiazol-4-yl(triphenyl)phosphonium chloride [6]. No depression of the melting point was observed on mixing samples of **XXIXb** prepared as described in *a* and *b*.

**Reaction of methyl 5-mercapto-2-phenyl-1,3-oxazole-4-carboxylate with sodium benzenesulfinate (*general procedure*).** To a solution of 0.001 mol of compound **XXIIa** in 10–15 ml of dimethylformamide we added an equimolar amount of anhydrous sodium benzenesulfinate. The mixture was stirred for 3 days at 20–25°C, the solvent was removed under reduced pressure, and the residue was treated with water and recrystallized from ethanol. Yield of bis-(4-methoxycarbonyl-2-phenyl-1,3-oxazol-5-yl) disulfide 75%, mp 154–155°C. The product was identical (according to the $^1$H NMR and IR data) to that obtained by oxidation of **XXIIa** with iodine [5].

## REFERENCES

1. Drach, B.S., Brovarets, V.S., and Smolii, O.B., *Sintezy azotsoderzhashchikh soedinenii na osnove*

*amidoalkiliruyushchikh agentov* (Syntheses of Nitrogen-Containing Compounds on the Basis of Amidoalkylating Agents), Kiev: Naukova Dumka, 1992, pp. 81–91.

2. Matsumura, K., Miyashita, O., Shimadzu, H., and Hashimoto, N., *Chem. Pharm. Bull.*, 1976, vol. 24, no. 5, p. 948.
3. Drach, B.S. and Mis'kevich, G.N., *Zh. Org. Khim.*, 1977, vol. 13, no. 7, p. 1398.
4. Lobanov, O.P., Martynyuk, A.P., and Drach, B.S., *Zh. Obshch. Khim.*, 1980, vol. 50, no. 10, p. 2248.
5. Vinogradova, T.K., Kisilenko, A.A., and Drach, B.S., *Zh. Org. Khim.*, 1982, vol. 18, no. 9, p. 1864.
6. Brovarets, V.S., Vydzhak, R.N., and Drach, B.S., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 5, p. 1053.
7. Kurg, V.V., Brovarets, V.S., and Drach, B.S., *Zh. Obshch. Khim.*, 1991, vol. 61, no. 4, p. 874.
8. Matsumura, K., Saraie, T., and Hashimoto, N., *Chem. Pharm. Bull.*, 1976, vol. 24, no. 5, p. 912.
9. Drach, B.S., Sviridov, E.P., Kisilenko, A.A., and Kirsanov, A.V., *Zh. Org. Khim.*, 1973, vol. 9, no. 9, p. 1818.
10. Drach, B.S., Sviridov, E.P., and Lavrenyuk, T.Ya., *Zh. Org. Khim.*, 1974, vol. 10, no. 6, p. 1271.
11. Drach, B.S. and Mis'kevich, G.N., *Zh. Org. Khim.*, 1978, vol. 14, no. 3, p. 501.
12. Drach, B.S. and Mis'kevich, G.N., *Zh. Org. Khim.*, 1974, vol. 10, no. 11, p. 2315.
13. Drach, B.S., Sviridov, E.P., and Shaturskii, Ya.P., *Zh. Obshch. Khim.*, 1974, vol. 44, no. 8, p. 1712.
14. Drach, B.S., Sviridov, E.P., and Kirsanov, A.V., *Zh. Obshch. Khim.*, 1975, vol. 45, no. 1, p. 12.