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Reactions of Aroxy- and Arylsulfanylacetic Acids and Their Esters with *N*-(2,2,2-Trichloro-1-hydroxyethyl)sulfonamides and -carboxamides

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Abstract—C-Amidoalkylation of aroxy- and arylsulfanylacetic acids and their methyl esters was effected by reaction with *N*-(2,2,2-trichloro-1-hydroxyethyl)sulfonamides and -carboxamides in the presence of methane- or trifluoromethanesulfonic acids as catalyst and solvent. The process is regioselective, and the substitution occurs at the *para*-position with respect to the heteroelement-containing group.

Introduction of additional pharmacophoric groups into molecules of aroxy- and arylsulfanylacetic acids and their derivatives may be very promising, for these compounds are known as plant growth regulators, herbicides, fungicides, and antiphlogistic and immunostimulating agents [1–6]. While studying the reactivity of CH=N groups having strong electron-acceptor substutuents [7], we have shown that aroxy-(arylsulfanyl)acetic acid esters readily react with accessible *N*-(2,2,2-trichloroethylidene)arenesulfonamides in the presence of oleum or (in some cases) boron trifluoride–diethyl ether complex [8] to give in good yields the corresponding 4-(1-arylsulfonylamino-2,2,2-trichloroethyl) derivatives at the aromatic ring. The synthesis of analogous products with the use of *N*-(polyhaloalkylidene)carboxamide was difficult, for these reagents are unstable and less accessible [7].

It is known that *N*-(2,2,2-trichloro-1-hydroxy)-arenesulfonamides, -carboxamides, and -carbamates, which are readily available from the corresponding amides and trichloroacetaldehyde (or via addition of water to *N*-trichloroethylidene derivatives), are effective C-amidoalkylating agents with respect to arenes in the presence of concentrated sulfuric acid [9–13]. We also found [8] that *N*-(2,2,2-trichloro-1-hydroxyethyl)arenesulfonamides do not react in such a way with methyl aroxy- and arylsulfanylacetates under the same conditions.

With the goal of obtaining compounds whose molecules contain fragments of aroxy- or arylsulfanylacetic acids together with polychloromethyl and amide groups, we examined reactions of accessible *N*-(2,2,2-trichloro-1-hydroxy)arenesulfonamides, -carboxamides, and -carbamates **Ia**–**Id** with aroxy- and arylsulfanylacetic acids and their methyl esters in the presence of sulfuric, methanesulfonic, and trifluoromethanesulfonic acids (Scheme 1). We failed to obtain the desired products by reactions of *N*-(2,2,2-trichloro-1-hydroxyethyl) derivatives **Ia**–**Id** with acids and esters **IIa**–**IIg** in the presence of sulfuric acid under the conditions ensuring successful amidoalkylation of arenes [9–11], including those having functional substituents [12, 13]. Presumably, this is explained by the poor solubility of aroxy(arylsulfanyl)acetic acid derivatives in sulfuric acid.

We have found that *N*-(2,2,2-trichloro-1-hydroxyethyl) amides **Ia**–**Id** readily react with acids and esters **IIa**–**IIg** in methane- or trifluoromethanesulfonic acid to give the corresponding 4-[2,2,2-trichloro-1-arylsulfonyl(acetyl, benzoyl, or ethoxycarbonyl)aminoethyl]-phenoxy(phenylsulfanyl)acetic acids and esters **III**–**XVII** (Scheme 1). We also examined the effect of temperature, reaction time, and amount and nature of the sulfonic acid on the reactions of acids and esters **IIa**–**IIg** with amides **Ia**–**Id**. The reactions were carried out with equimolar amounts of the reactants at 20°C or on heating to 50°C, and the reaction time was varied from 3 h to 3 days. We used catalytic amounts (10–60 mol %) of methanesulfonic and trifluoromethanesulfonic acids in chloroform or these com-

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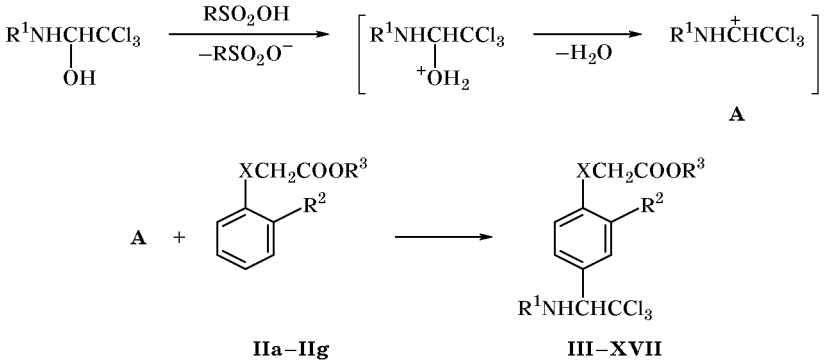
Scheme 1.



R = Me, CF_3; **I**, R^1 = 4-$ClC_6H_4SO_2$ (**a**), EtOC(O) (**b**), MeC(O) (**c**), PhC(O) (**d**); **II**, X = O, $R^2 = R^3$ = H (**a**); X = O, R^2 = H, R^3 = Me (**b**); X = O, $R^2 = R^3$ = Me (**c**); X = O, R^2 = Cl, R^3 = Me (**d**); X = S, $R^2 = R^3$ = H (**e**); X = S, R^2 = H, R^3 = Me (**f**); X = S, $R^2 = R^3$ = Me (**g**); **III**, X = O, R^1 = 4-$ClC_6H_4SO_2$, R^2 = H, R^3 = Me; **IV**, X = O, R^1 = EtOC(O), R^2 = H, R^3 = Me; **V**, X = O, R^1 = MeC(O), R^2 = H, R^3 = Me; **VI**, X = O, R^1 = PhC(O), R^2 = H, R^3 = Me; **VII**, X = O, R^1 = EtOC(O), $R^2 = R^3$ = Me; **VIII**, X = O, R^1 = PhC(O), $R^2 = R^3$ = Me; **IX**, X = O, R^1 = PhC(O), R^2 = Cl, R^3 = Me; **X**, X = O, R^1 = 4-$ClC_6H_4SO_2$, $R^2 = R^3$ = H; **XI**, X = O, R^1 = EtOC(O), $R^2 = R^3$ = H; **XII**, X = S, R^1 = 4-$ClC_6H_4SO_2$, R^2 = H, R^3 = Me; **XIII**, X = S, R^1 = EtOC(O), R^2 = H, R^3 = Me; **XIV**, X = S, R^1 = MeC(O), R^2 = H, R^3 = Me; **XV**, X = S, R^1 = PhC(O), R^2 = H, R^3 = Me; **XVI**, X = S, R^1 = EtOC(O), $R^2 = R^3$ = Me; **XVII**, X = S, R^1 = 4-$ClC_6H_4SO_2$, $R^2 = R^3$ = H.

pounds were taken in a 3–6-fold excess with respect to **I** and **II**, so that they played the role of solvent. Also a mixture of sulfonic acid (100 to 200 mol % relative to **I** and **II**) with chloroform at a volume ratio of 1 : 1 was used.

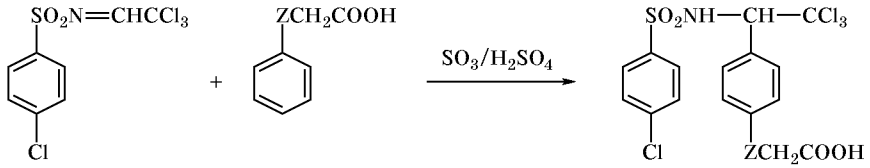
Amides **Ia**–**Id** failed to react with compounds **IIa**–**IIg** in chloroform in the presence of 10–60 mol % of methane- or trifluoromethanesulfonic acid both at 20 and at 50°C even when the reaction was prolonged to 3 days. Apart from the initial reactants, we isolated products of decomposition of *N*-(2,2,2-trichloro-1-hydroxyethyl) derivatives **Ia**–**Id**, the corresponding unsubstituted amides: 4-chlorobenzenesulfonamide (**XVIIIa**), ethyl carbamate (**XVIIIb**), acetamide (**XVIIIc**), and benzamide (**XVIIId**). The fraction of amides **XVIII** increased with rise in temperature and reaction time: at 20°C (72 h), the yield of **XVIII** was 5–10%, and at 50°C (5–72 h), 50%.

When the reaction was carried out in a 1 : 1 (by volume) mixture of methanesulfonic acid and chloroform at a $MeSO_3H$-to-**I**(**II**) molar ratio of 1 : 1 to 1 : 3–4 (20°C, 10–20 h), target products **III**–**XVII** were formed in up to 50% yield. Also, up to 10% of amides **XVIIIa**–**XVIIId** and up to 5% of initial reactants (hydroxyethyl amides **I** and esters or acids **II**) were isolated. Increase of the reaction time to 72 h favored formation of amides **XVIIIa**–**XVIIId**. Heating of the reaction mixture to 50°C resulted in formation of up to 50% of amides **XVIIIa**–**XVIIId**, while the yield of target products **III**–**XVII** did not exceed 50%.

A considerable success was reached by carrying out the reaction in methanesulfonic acid, the molar ratio **II**–$MeSO_3H$ being ~1 : 6 (20°C, 3–10 h). In this case, products **III**–**XVII** were formed in 75–93% yield (method *A*). The use of trifluoromethanesulfonic acid as solvent (molar ratio **II**–CF_3SO_3H 1 : 1–4; 20 to 50°C; 3 to 72 h) did not increase the yield of **III**–**XVII**, but the corresponding amides **XVIIIa**–**XVIIId** were obtained in 5–80% yield. We succeeded in effecting successful amidoalkylation of compounds **IIa**–**IIg** with amides **Ia**–**Id** in a mixture of trifluoromethanesulfonic acid with chloroform. The maximal yields of compounds **III**–**XVII** (75–94%) and the minimal yields (0.5–5%) of amides **XVIIIa**–**XVIIId** were attained when the reaction was carried out at 20°C (3–5 h) in a mixture of equal volumes of trifluoromethanesulfonic acid (molar ratio CF_3SO_3H–**II** 2–3 : 1) and chloroform (method *B*).

Thus, using methane- or trifluoromethanesulfonic acid as solvent or co-solvent in the reactions of *N*-(2,2,2-trichloro-1-hydroxyethyl)amides **Ia**–**Id** with aroxy(arylsulfanyl)acetic acids or their esters **IIa**–**IIg** we succeeded in developing a preparative procedure for synthesizing difficultly accessible functionalized aroxy- and arylsulfanylacetic acid derivatives **III**–**XVII** in 75–94% yield. We believe that these reactions are favored by homogeneous reaction medium (acids and esters **II** are readily soluble in methane- and trifluoromethanesulfonic acids [14]), as well as by the strong protonating ability of these sulfonic acids. In fact, trifluoromethanesulfonic acid (H_0 = 14.1) is

Scheme 2.



X, XVII

X, Z = O; **XVII**, Z = S.

stronger than sulfuric acid (H_0 12.1) and 3 : 1 H_2SO_4–SO_3 mixture (H_0 = 13.6) [15], and the acididty of anhydrous methanesulfonic acid is likely to be comparable with that of aqueous sulfuric acid [16].

Compounds **X** and **XVII** were also obtained in up to 70% yield by reaction of *N*-(2,2,2-trichloroethylidene)-4-chlorobenzenesulfonamide with acids **IIa** and **IIe**, respectively, under the conditions analogous to those reported in [8] (Scheme 2, method *C*). Here, no products of nucleophilic addition of acids **IIa** and **IIe** at the C=N bond were detected.

Products **III**–**XVII** are crystalline substances with no odor. They are readily soluble in alcohol, acetone, and DMSO, sparingly soluble in chloroform and ether, and insoluble in water. Their structure was confirmed by elemental analysis (Table 1) and ^{1}H NMR and IR spectroscopy (Table 2). The properties of previously known compounds **III** and **XII** were consistent with published data [8].

The IR spectra of **III**–**XVII** contain strong absorption bands due to vibrations of the NH, SO_2, and COOH groups (compound **X**, **XII**, and **XVII**), COOMe groups (**III**–**IX** and **XII**–**XVI**), aromatic C=C and C–H bonds, and aliphatic C–H bonds (Table 2). Compounds **III**–**XVII** characteristically show in the ^{1}H NMR spectra doublet signals from the NH and CH protons (J = 10–11 Hz) and singlets from protons of the XCH_2 and $COOCH_3$ groups (Table 2). Aromatic protons in **III**–**VI** and **X**–**XVII** give rise to an *AA′BB′* spin system, which indicates formation of *para*-substituted products. The presence of a singlet and two doublets from aromatic protons in the spectra of compounds **VII**–**IX** and **XVI** suggests *o*,*p*-substitution pattern in their molecules. The ^{1}H NMR spectra of **V** and **XIV** contain singlets from the methyl group, and compounds **IV**, **VII**, **X**, **XIII**, **XVI** give rise to a characteristic triplet–quartet system from the ethoxy group in the carbamate fragment. In the spectra of **V**, **VIII**, and **XV**, signals from aromatic protons of the benzoylamino group were also present.

The SCH_2 protons in molecule **XVI** are magnetically nonequivalent, and they appear in the ^{1}H NMR spectrum as an *AB* quartet at δ 3.81 and 3.72 ppm, J_{AB} = 14.9 Hz). Presumably, the reason is restricted rotation about the C–S bond due to steric interactions between the $MeOC(O)CH_2CS$ group and *o*-methyl group and the presence of an asymmetric center ($CHCCl_3$) in the *para*-position of the aromatic ring. No such effect is observed for oxygen analog **VII**.

Thus, using methane- or trifluoromethanesulfonic acid as solvent and catalyst, we succeeded in effecting regioselective C-amidoalkylation of aroxy- and arylthioacetic acids and their methyl esters with *N*-(2,2,2-trichloro-1-hydroxyethyl) derivatives of carboxamides, sulfonamides, and ethyl carbamate.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400 (400 and 100.6 MHz, respectively) and Jeol FX-90Q spectrometers (90 and 84 MHz, respectively); samples were examined as 5–10% solutions containing HMDS as internal reference. The IR spectra were measured in KBr using a Specord IR75 spectrometer.

N-(2,2,2-Trichloro-1-hydroxyethyl) amides **Ia**–**Id** were synthesized from the corresponding amides and trichloroacetaldehyde [17] or by addition of water to Schiff bases derived from trichloroacetaldehyde [7]. *N*-(2,2,2-Trichloroethylidene)-4-chlorobenzenesulfonamide was obtained from 4,*N*,*N*-trichlorobenzenesulfonamide and trichloroethylene [18].

General procedure for the preparation of compounds III–XVII. *Method A.* Compound **Ia**–**Id**, 0.01 mol, was dissolved at 10–15°C under stirring in 4 ml (0.06 mol) of methanesulfonic acid. After 5–10 min, 0.01 mol of compound **IIa**–**IIg** was added. The mixture was stirred for 15 min at 10–15°C and for 5 h at room temperature. When the reaction was complete, 100 ml of water was added, and the precipitate was filtered off, washed with water until neutral washings, and dried in air.

Method B. Compound **Ia**–**Id**, 0.01 mol, was dissolved under stirring in 2 ml of chloroform. The solu-

Table 1. Yields, melting points, and elemental analyses of compounds **III**–**XVII**

Comp. no.	Yield, %		mp, °C	Found, %					Formula	Calculated, %				
	A	*B*		C	H	Cl	N	S		C	H	Cl	N	S
III	92	90	152–155	41.73	3.21	28.72	2.76	7.28	$C_{17}H_{15}Cl_4NO_5S$	41.91	3.10	29.11	2.88	6.58
IV	89	91	116–117	44.12	4.25	26.99	3.56	–	$C_{14}H_{16}Cl_3NO_5$	43.72	4.19	27.65	3.64	–
V	85	88	138–142	43.98	4.03	29.19	4.06	–	$C_{13}H_{14}Cl_3NO_4$	44.03	3.98	29.99	3.95	–
VI	87	83	126–128	52.17	3.91	24.97	3.16	–	$C_{18}H_{16}Cl_3NO_4$	51.88	3.87	25.52	3.36	–
VII	78	77	126–131	45.61	4.43	25.97	3.42	–	$C_{15}H_{18}Cl_3NO_5$	45.19	4.55	26.68	3.51	–
VIII	80	83	150–154	53.09	4.12	24.19	3.36	–	$C_{19}H_{18}Cl_3NO_4$	52.98	4.21	24.69	3.25	–
IX	78	80	120–124	47.78	3.43	31.04	3.01	–	$C_{18}H_{15}Cl_4NO_4$	47.92	3.35	31.43	3.10	–
X	90	94	165–171	40.54	2.97	29.68	3.09	7.07	$C_{16}H_{13}Cl_4NO_5S$	40.62	2.77	29.97	2.96	6.78
XI	93	91	120–122	41.95	3.69	28.07	3.67	–	$C_{13}H_{14}Cl_3NO_5$	42.13	3.81	28.70	3.78	–
XII	89	90	114–118	40.08	3.05	27.99	2.67	13.05	$C_{17}H_{15}Cl_4NO_4S_2$	40.57	3.00	28.18	2.78	12.74
XIII	87	87	98–102	41.79	3.92	26.05	3.46	8.19	$C_{14}H_{16}Cl_3NO_4S$	41.96	4.02	26.54	3.50	8.00
XIV	82	84	155–156	42.43	3.92	28.48	3.80	8.96	$C_{13}H_{14}Cl_3NO_3S$	42.12	3.81	28.69	3.78	8.65
XV	83	80	118–122	50.09	3.67	24.15	3.44	7.84	$C_{18}H_{16}Cl_3NO_3S$	49.96	3.73	24.58	3.24	7.41
XVI	75	78	163–166	43.00	4.39	25.65	3.35	7.70	$C_{15}H_{18}Cl_3NO_4S$	43.44	4.37	25.65	3.38	7.73
XVII	90	94	150–154	39.23	2.86	28.87	2.69	13.41	$C_{16}H_{13}Cl_4NO_4S_2$	39.28	2.68	28.99	2.86	13.11

tion was cooled to 10–15°C, 2 ml (0.02 mol) of trifluoromethanesulfonic acid was added, the mixture was stirred for 5–10 min, and 0.01 mol of compound **IIb** was added. The mixture was stirred for 15 min at 10–15°C and for 5 h at room temperature. Chloroform was evaporated, 200 ml of water was added to the residue, and the precipitate was filtered off, washed with water until neutral washings, and dried in air.

Method C. *N*-(2,2,2-Trichloroethylidene)-4-chlorobenzenesulfonamide, 3.21 g (0.01 mol) (prepared from 4,*N*,*N*-trichlorobenzenesulfonamide and trichloroethylene as described in [17]), was dissolved in 8 ml of dry chloroform, and 0.01 mol of compound **IIa** or **IIe** was added to the solution in a stream of dry argon. The mixture was cooled to 10°C, and 1 ml of oleum (2 to 20% of SO_3) was added dropwise under vigorous stirring. The mixture was stirred for 15 min at 10°C and for 3 h at room temperature. The oily material was separated from the mixture by decanting, washed with water (3 × 20 ml) and diethyl ether (3 × 10 ml), and dried in air.

Methyl 4-[2,2,2-trichloro-1-(4-chlorophenylsulfonylamino)ethyl]phenoxyacetate (III) was obtained according to methods *A* and *B* from 3.39 g (0.01 mol) of compound **Ia** and 1.66 g (0.01 mol) of methyl phenoxyacetate (**IIb**). Yield 4.48 g (*A*), 4.38 g (*B*).

Methyl 4-[2,2,2-trichloro-1-(ethoxycarbonylamino)ethyl]phenoxyacetate (IV) was synthesized according to methods *A* and *B* from 2.36 g (0.01 mol) of compound **Ib** and 1.66 g (0.01 mol) of methyl phenoxyacetate (**IIb**). Yield 3.43 g (*A*), 3.50 g (*B*).

Methyl 4-(1-acetylamino-2,2,2-trichloroethyl)-phenoxyacetate (V) was synthesized according to methods *A* and *B* from 2.06 g (0.01 mol) of compound **Ic** and 1.66 g (0.01 mol) of ester **IIb**. Yield 3 g (*A*), 3.12 g (*B*).

Methyl 4-(1-benzoylamino-2,2,2-trichloroethyl)-phenoxyacetate (VI) was synthesized according to methods *A* and *B* from 2.68 g (0.01 mol) of compound **Id** and 1.66 g (0.01 mol) of ester **IIb**. Yield 3.63 g (*A*), 3.46 g (*B*).

Methyl 4-[2,2,2-trichloro-1-(ethoxycarbonylamino)ethyl]-2-methylphenoxyacetate (VII) was synthesized according to methods *A* and *B* from 2.36 g (0.01 mol) of compound **Ib** and 1.8 g (0.01 mol) of methyl 2-methylphenoxyacetate (**IIc**). Yield 3.11 g (*A*), 3.07 g (*B*).

Methyl 4-(1-benzoylamino-2,2,2-trichloroethyl)-2-methylphenoxyacetate (VIII) was synthesized according to methods *A* and *B* from 2.68 g (0.01 mol) of compound **Id** and 1.8 g (0.01 mol) of ester **IIc**. Yield 3.44 g (*A*), 3.57 g (*B*).

Methyl 4-(1-benzoylamino-2,2,2-trichloroethyl)-2-chlorophenoxyacetate (IX) was obtained according to methods *A* and *B* from 2.68 g (0.01 mol) of com-

Table 2. IR and ^{1}H NMR spectra of compounds **III**–**XVII**

Comp. no.	IR spectrum, ν, cm^{-1}						^{1}H NMR spectrum,[a] δ, ppm (*J*, Hz)					
	COC	C=C	C=O	C–H aliph.	=C–H arom.	N–H	XCH_2 (s)	CH (d)	H_{arom}	NH (d)	R^1	R^3 (s)
III	1160,[b] 1330[b]	1430, 1510, 1610	1760	2930, 2970	3060, 3090	3270	4.76	5.21 (10.5)	7.42 d, 6.76 d (6.9)	9.25 (10.5)	7.60 d, 7.39 d (6.8)	3.74
IV	1180, 1250	1510, 1610	1720	2950, 2990	3070	3340	4.80	5.52 (10.2)	7.62 d, 6.92 d (8.8)	8.62 (10.2)	1.18 t, 4.08 q (7.1)	3.69
V	1190, 1230, 1250	1520, 1610, 1680	1750	2910, 2940, 2960	3040, 3070	3350	4.81	5.84 (10.0)	7.58 d, 6.94 d (8.3)	9.04 (10.0)	1.97 s	3.69
VI	1200, 1260	1520, 1630	1760, 1770	2860	3060, 3080	3300	4.80	6.27 (15.3)	7.81 d, 7.00 d (8.7)	9.04 (15.3)	7.91 d (7.3), 7.57 m, 7.47 m	3.75
VII	1160, 1250	1500, 1510, 1610	1720, 1760	2950, 2980	3060, 3090	3250	4.83	5.49 (10.0)	7.59 s (2-H), 7.47 d (5-H), 6.82 d (6-H, 8.6), 2.20 s (CH_3)	8.56 (10.0)	1.18 t, 4.07 q (7.1)	3.70
VIII	1140, 1260	1520, 1640	1740	2860, 2920, 2950	3050, 3090	3310	4.85	6.09 (9.9)	7.66 s (2-H), 7.50 d (5-H, 8.5), 6.86 d (6-H), 2.22 s (CH_3)	9.26 (9.9)	7.84 d, 7.57 m, 7.48 m	3.69
IX	1080, 1220, 1280	1500, 1520, 1610	1740	2930, 2950	3060, 3090	3310	4.97	6.18 (9.8)	8.09 s (2-H), 7.72 d (5-H, 8.7), 7.09 d (6-H, 8.7)	9.35 (9.8)	7.84 d, 7.59 t, 7.50 t	3.71
X	1170,[b] 1340,[b] 1240	1510, 1590, 1610	1740	2920, 2950	3070, 3090	3250	4.68	5.22 (10.6)	7.44 d, 6.77 d (8.8)	7.92 (10.6)	7.57 d, 7.44 d (6.8)	–
XI	1170, 1240	1510, 1590, 1610	1700	2920, 2950, 2980	3070	3410	4.72	5.62 (10.4)	7.67 d, 6.97 d (11.9)	7.59 (10.4)	1.17 t, 4.07 q (7.1)	–
XII	1170,[b] 1330[b]	1470, 1590	1710	2850, 2950	3090	3245	3.93	5.23 (10.3)	7.43 d, 7.07 d (8.1)	9.26 (10.3)	7.65 d, 7.41 d (8.5)	3.66
XIII	1150, 1240	1510, 1540	1710	2850, 2920	3030	3300	3.93	5.62 (10.5)	7.70 d, 7.34 d (8.4)	8.67 (10.5)	1.19 t, 4.10 q (7.1)	3.63
XIV	1160, 1270	1530, 1610	1760	2860, 2900	3050	3310	3.92	6.05 (10.3)	7.60 d, 7.51 d (8.4)	9.09 (10.3)	1.98 s	3.69
XV	1150, 1280	1480, 1510, 1580	1740[a]	2850, 2910, 2950	3050	3300	4.02	6.22 (10.3)	7.81 d, 7.36 d (8.3)	9.41 (10.3)	7.85 d, 7.57 t, 7.50 m	3.68

Table 2. (Contd.)

Comp. no.	IR spectrum, ν, cm^{-1}						^1H NMR spectrum,[a] δ, ppm (*J*, Hz)					
	COC	C=C	C=O	C−H aliph.	=C−H arom.	N−H	XCH_2 (s)	CH (d)	H_{arom}	NH (d)	R^1	R^3 (s)
XVI	1250	1520	1730	2950, 2970	3030, 3050	3330	3.81,[c] 3.72[c]	6.58 (10.3)	7.84 s (2-H), 7.51 d (6-H), 7.23 d (5-H), 2.33 s (CH_3)	8.57 (10.3)	1.22 t, 4.09 q (7.1)	3.59
XVII	1170,[b] 1350[b]	1470, 1580, 1590, 1600	1710	2900	3060, 3090	3250	3.78	5.24 (10.7)	7.46 d, 7.22 d (8.3)	7.98 (10.7)	7.58 d, 7.33 d (8.6)	–

[a] The ^1H NMR spectra of compounds **VI**, **X**, **XI**, and **XVII** were recorded in acetone-d_6, and of the others, in DMSO-d_6.
[b] νSO_2.
[c] *AB*-quartet, J = 14.9 Hz.

pound **Id** and 2.0 g (0.01 mol) of methyl 2-chlorophenoxyacetate (**IId**). Yield 3.52 g (*A*), 3.60 g (*B*).

4-[2,2,2-Trichloro-1-(4-chlorophenylsulfonylamino)ethyl]phenoxyacetic acid (X) was synthesized according to methods *A* and *B* from 3.39 g (0.01 mol) of compound **Ia** and 1.52 g (0.01 mol) of phenoxyacetic acid (**IIa**) or according to method *C* from 3.21 g (0.01 mol) of *N*-(2,2,2-trichloroethylidene)-4-chlorobenzenesulfonamide. Yield 4.26 g (*A*), 4.44 g (*B*), 4.25 g (*C*).

4-[2,2,2-Trichloro-1-(ethoxycarbonylamino)ethyl]phenoxyacetic acid (XI) was synthesized according to methods *A* and *B* from 2.36 g (0.01 mol) of compound **Ib** and 1.52 g (0.01 mol) of acid **IIa**. Yield 3.44 g (*A*), 3.36 g (*B*).

Methyl 4-[2,2,2-trichloro-1-(4-chlorophenylsulfonylamino)ethyl]phenylsulfanylacetate (XII) was synthesized according to methods *A* and *B* from 3.39 g (0.01 mol) of compound **Ia** and 1.82 g (0.01 mol) of methyl phenylsulfanylacetate (**IIf**). Yield 4.47 g (*A*), 4.52 g (*B*).

Methyl 4-[2,2,2-trichloro-1-(ethoxycarbonylamino)ethyl]phenylsulfanylacetate (XIII) was synthesized according to methods *A* and *B* from 2.36 g (0.01 mol) of compound **Ib** and 1.82 g (0.01 mol) of methyl phenylsulfanylacetate (**IIf**). Yield 3.48 g (*A*), 3.48 g (*B*).

Methyl 4-(1-acetylamino-2,2,2-trichloroethyl)-phenylsulfanylacetate (XIV) was synthesized according to methods *A* and *B* from 2.06 g of compound **Ic** and 1.82 g (0.01 mol) of ester **IIf**. Yield 3.03 g (*A*), 3.11 g (*B*).

Methyl 4-(1-benzoylamino-2,2,2-trichloroethyl)-phenylsulfanylacetate (XV) was synthesized according to methods *A* and *B* from 2.68 g (0.01 mol) of compound **Id** and 1.82 g (0.01 mol) of ester **IIf**. Yield 3.58 g (*A*), 3.46 g (*B*).

Methyl 4-[2,2,2-trichloro-1-(ethoxycarbonylamino)ethyl]-2-methylphenylsulfanylacetate (XVI) was synthesized according to methods *A* and *B* from 2.36 g (0.01 mol) of compound **Ib** and 1.96 g (0.01 mol) of methyl 2-methylphenylsulfanylacetate (**IIg**). Yield 3.10 g (*A*), 3.23 g (*B*).

4-[2,2,2-Trichloro-1-(4-chlorophenylsulfonylamino)ethyl]phenylsulfanylacetic acid (XVII) was synthesized according to methods *A* and *B* from 3.39 g (0.01 mol) of compound **Ia** and 1.68 g (0.01 mol) of phenylsulfanylacetic acid (**IIe**) or according to method *C* from 3.21 g (0.01 mol) of *N*-(2,2,2-trichloroethylidene)-4-chlorobenzenesulfonamide. Yield 3.96 g (*A*), 3.96 g (*B*), 4.20 g (*C*).

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