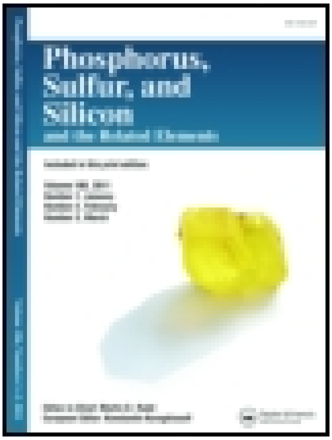

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UNEXPECTED DESULFONATION OF α-PHENYLSULFONYL ENAMINOACRYLATES DURING THEIR CYCLISATION TO NEW N-ARYL 4H-1,4-BENZOTHIAZINE-l,l-DIOXIDES

Simón E. López [a] , Jaime Charris [c] , Neudo Urdaneta [a] , Carlos E. Canelón [a] , José Salazar [a] , Julio Herrera [b] & Jorge E. Angel [d]

[a] Luboratorio de Quimica Orgánica , 210

[b] Laboratorio de Resonanica Magnética Nuclear, Departamento de Química , Universidad Simón Bolivar , Valle de Sartenejas, Caracas 1080-A, Aparatado, 89000, Venczuela

[c] Laboratorio de Sintesis Orgánica, piso, I Facultad de Farmacia , Universidad Central de Venzuela , Los Chaguaramos, Caracas, 1051-A, Venzuela

[d] Laboratorio de Sintesis Orgánica y Diseño Molecular, Departamento de Química, Módulo II. Facultad Experimental de Ciencias , Universidad del Zulia, Maracaibo , Venezuela

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UNEXPECTED DESULFONATION OF α-PHENYLSULFONYL ENAMINOACRYLATES DURING THEIR CYCLISATION TO NEW N-ARYL 4*H*-1,4-BENZOTHIAZINE-1,1-DIOXIDES

SIMÓN E. LÓPEZ[a]*, JAIME CHARRIS[c], NEUDO URDANETA[a], CARLOS E. CANELÓN[a], JOSÉ SALAZAR[a], JULIO HERRERA[b] and JORGE E. ANGEL[d]

[a]Laboratorio de Química Orgánica 210 and [b]Laboratorio de Resonancia Magnética Nuclear, Departamento de Química, Universidad Simón Bolívar, Valle de Sartenejas, Caracas 1080-A, Apartado 89000, Venezuela, [c]Laboratorio de Sintesis Orgánica, piso 1, Facultad de Farmacia, Universidad Central de Venezuela, Los Chaguaramos, Caracas 1051-A, Venezuela and [d]Laboratorio de Síntesis Orgánica y Diseño Molecular, Departamento de Química, Módulo II, Facultad Experimental de Ciencias, Universidad del Zulia, Maracaibo, Venezuela

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An unexpected desulfonation of α-phenylsulfonyl-enaminoacrylates occurred during their cyclisation to novel 6,7-dichloro-N-aryl-4*H*-1,4-benzothiazine-1,1-dioxides using potassium carbonate and silver nitrate in DMF. This last cyclisation step was not completed in five hours of reaction but, instead of higher yields of the desired cyclic 4*H*-benzothiazines, a mixture of the above mentioned target compounds and desulfonated N-formyl-2-aryl-enaminoacrylates were obtained.

Keywords: 4H-1,4-Benzothiazine-1,1-dioxides; N-formyl-2-aryl-enaminoacrylates; desulfonation; cyclization

In connection with our research program directed toward the synthesis of novel 1,4-benzothiazines and phenothiazines with potential biological activity,[1–3] we have recently described an improved procedure for the preparation of N-aryl substituted 4*H*-1,4-benzothiazine-1,1-dioxide derivatives using potassium carbonate in DMF and silver nitrate as a catalyst.[3]

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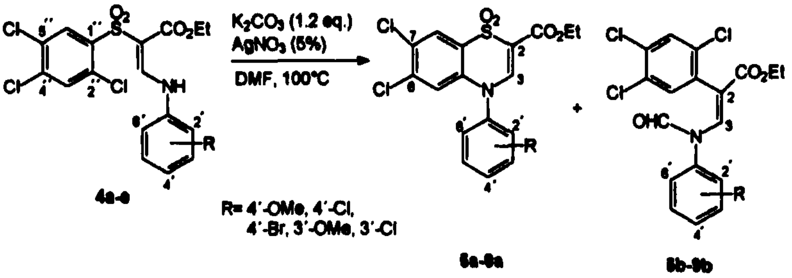
* Corresponding author: Fax: 582–906 39 61; e-mail: slopez@usb.ve

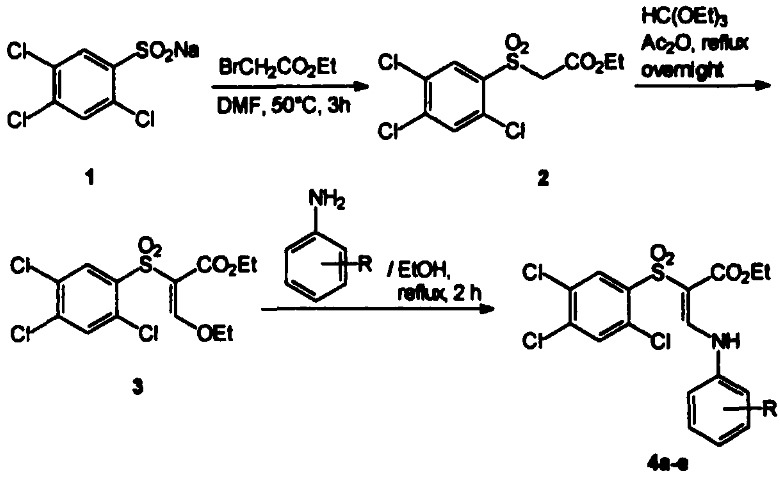
Although there are a few methodologies for the synthesis of N-alkyl-4*H*-1,4-benzothiazines,[4–6] only two procedures have been described for the preparation of N-aryl derivatives.[2,3] In view that our procedure offered high yields of desired benzothiazine products at short reaction times and target compounds were easily purified by recrystallization,[3] we decided to investigate the scope of this reaction varying the substitution pattern on the benzene ring linked to the sulfur atom of the corresponding acrylate. This paper reports an unexpected desulfonation and formylation of the precursor α-phenylsulfonyl-enaminoacrylates **4a-e** during their cyclisation to new 4*H*-1,4-benzothiazines **5a-9a** (Scheme 1).



SCHEME 1

Starting from sodium 2,4,5-trichlorobenzene-sulfinate **1**, the precursor α-phenylsulfonyl enaminoacrylates **4a-e** were easily prepared in a 3-step procedure (Scheme 2). Thus, the treatment of **1** with ethylbromoacetate in DMF at 50°C for three hours afforded ethyl-2,4,5-trichlorophenyl-sulfonylacetate **2**, which was further reacted with triethyl orthoformate in acetic anhydride under reflux overnight yielding the enol ether **3**. This last intermediate was allowed to react as a crude with a substituted aniline in dry ethanol under reflux for two hours using a catalytic amount of concentrated sulphuric acid, yielding the required *E*-α-phenylsulfonyl-enaminoacrylates **4a-e** as sole products.

Finally, we thought that **4a-e** could be easily cyclisized using 1.2 eq of potassium carbonate and 5% silver nitrate in hot DMF as previously described for related acrylates,[3] but instead of higher yields of desired cyclic products **5a-9a**, only moderate yields of these benzothiazines and additionally unexpected N-formyl 2-aryl-enaminoacrylates **5b-9b** were obtained. These last acrylates showed the absence of expected SO_2



SCHEME 2

stretching bands in the IR spectra and their stereochemistry was determined through two dimensional NMR spectroscopy. Surprisingly, the formation of these desulfonated acrylates competes with the cyclisation process, lowering the yields of target compounds. Although these byproducts were obtained at minor amounts (Table I), the results here presented suggest that the presence of an additional chlorine atom at position 5″ of the coesponding precursor acrylates (**4a-e**) is unfavourable for the cyclisation to take place in higher yields. We postulate that this chlorine atom may account for an elevation of the transition state energy required for cyclisation, giving a chance for the desulfonation and formylation to occur. Thermal desulfonation of 2-acylaminobenzenesulfonamides during their cyclisation to 2*H*-1,2,4-benzothiadiazine-1,1-dioxides was reported some years ago, giving the conesponding 2-acylaminobenzenes in addition to the expected benzothiadiazines.[7] Coincidentally, the above mentioned sulfonamides have two chlorine atoms with the same substitution pattern as that as our precursor acrylates (positions 4“ and 5” respectively in **4a-e**). While previously supposed, silver nitrate may act as a Lewis acid catalyst in the cyclisation step;[8] but we have not yet attempted to know its possible role in the competitive desulfonation. However, a more extensive and detailed work concerning to these observations is ongoing in our research group and will be published elsewhere.

TABLE I Cyclization of 4a-e to give 5a-9a and 5b-9b

Entry	*R*	*a/b ratio*[a]	*Compd. No (% yield)*	
4a	4'-OMe	75/25	**5a**(68)	**5b**(23)
4b	4'-Cl	71/29	**6a**(63)	**6b**(26)
4c	4'-Br	65/35	**7a**(52)	**7b**(28)
4d	3'-OMe	73/27	**8a**(51)	**8b**(19)
4e	3'-Cl	69/31	**9a**(47)	**9b**(21)

a. Determined by the ^{1}H NMR spectra.

EXPERIMENTAL

Melting points were determined with a Fischer-Johns micro hot-stage apparatus. The IR spectra were recorded as KBr pellets using a BIO-Rad FT/IR 6000 Excalibur Series spectrometer. Proton NMR spectra (NMR) were recorded either on a JEOL Eclipse (270 MHz) or a JEOL Eclipse Plus (400 MHz) spectrometer; δ values in ppm relative to tetramethylsilane are given. When reported, mass spectra were recorded on a Hewlett-Packard HP5971A Mass Selective Detector with EI(70 eV) connected to a gas chromatograph HP5970 Series II. Elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA, USA); the results fell in the range ± 0.4% of the required theoretical values. Silica gel plates ALUGRAM® SIL G/UV$_{254}$ (Macherey-Nagel GmbH & Co., Germany) were used for TLC testing. Column chromatography was performed with Kieselsgel 60 (70–230 mesh, Merck, Darmstadt, Germany) and hexane-ethyl acetate (8:2) as eluant Reagents were obtained from Aldrich (USA) and used without further purification. Solvents were distilled prior to use. Sodium 2,4,5-trichlorobenzene sulfinate **1** was prepared according to the literature procedure.[9]

Ethyl 2,4,5-trichlorophenyl-sulfonylacetate 2

Sodium 2,4,5-trichlorobenzenesulfinate **1** (3.6 g, 13.5 mmol) was dissolved in DMF (35 mL), then ethyl bromoacetate (2.3 g, 13.8 mmol) was slowly added and the reaction mixture was stirred at 50°C for three hours.

The mixture was allowed to cool at room temperature, poured into ice-crushed water giving a white precipitate, which was further filtered, washed twice with water and dried under vacuo. Yield: 3.5 g (78%) after recrystallization from ethanol-water (6:4), mp 75–76 °C. IR (KBr, cm^{-1}): $\nu = 1730$ (C=O, ester); 1330, 1300 (SO_2); 1160, 1090 (SO_2). MS (EI): $m/z = 332$ (M^+). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.19$ (t, 3H, CH_3), 4.14 (q, 2H, O-CH_2-), 4.40 (s, 2H, methylene CH_2), 7.68 (s, 1H, 3'-H), 8.18 (s, 1H, 6'-H).

Anal. Calcd. for $C_{10}H_9Cl_3O_4S$: C, 36.22; H, 2.74.
Found: C, 35.96; H, 2.66.

Ethyl 2-(2,4,5-trichloro-phenylsulfonyl)-3-(substituted-anilino)-acrylates 4a-e

General procedure

A mixture of **2** (1.5 g, 4.5 mmol), acetic anhydride (0.69 g, 6.8 mmol) and triethylorthoformate (1.6 g, 10.8 mmol) was stirred under reflux using a Dean Stark trap for 3 h. The solvent was then removed under vacuo and the remaining brown enol-ether oil was directly employed as a crude for the next step. This latter crude was dissolved in dry ethanol (40 mL), a substituted aniline (4.5 mmol) was slowly added and the mixture was stirred for 10 min at room temperature; subsequently, 1 drop of concentrated sulphuric acid (99%) was additionally added and the resulting mixture was then stirred under reflux for 2 h. After cooling at room temperature, the obtained solid was filtered, washed with ethanol, and dried under vacuo giving the expected enamino-acrylates **4a-e**.

Ethyl 2-(2,4,5-trichloro-phenylsulfonyl)-3-(4-methoxyanilino)-acrylate 4a

Yield: 1.5 g (71 %) *after* recrystallization from ethanol, mp: 201–202 °C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.15$ (t, 3H, CH_3), 3.81 (s, 3H, OCH_3), 4.11 (q, 2H, O-CH_2-), 6.92 (d, 2H, 2'-H, 6'-H, J=8.8 Hz), 7.11 (d, 2H, 3'-H, 5'-H, J=8.8 Hz), 7.54 (s, 1H, 3'-H), 8.35 (s, 1H, 6'-H), 8.49 (d, 1H, vinyl CH, J=13.9 Hz), 10.70 (d, 1H, NH, J=13.9 Hz).

Anal. Calcd. for $C_{18}H_{16}Cl_3NO_5S$: C, 46.52; H, 3.47; N, 3.01.
Found: C, 46.21; H, 3.24, N, 3.12.

Ethyl 2-(2,4,5-trichloro-phenylsulfonyl)-3-(4-chloroanilino)-acrylate 4b

Yield: 1.42 g (67 %) *after* recrystallization from ethanol, mp: 208–209 °C. IR (KBr, cm^{-1}): $\nu = 1695$ (C=O, ester); 1320, 1290 (SO_2); 1130, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.15$ (t, 3H, CH_3), 4.12 (q, 2H, O-CH_2-), 7.12 (d, 2H, 2′-H, 6′-H, J=8.8 Hz), 7.38 (d, 2H, 3′-H, 5′-H, J=8.8 Hz), 7.55 (s, 1H, 3′-H), 8.35 (s, 1H, 6′-H), 8.55 (d, 1H, vinyl CH, J=13.7 Hz), 10.74 (d, 1H, NH, J=13.7 Hz).

Anal. Calcd. for $C_{17}H_{13}Cl_4NO_4S$: C, 43.52; H, 2.79; N, 2.99.

Found: C, 43.69; H, 2.84; N, 3.05.

Ethyl 2-(2,4,5-trichloro-phenylsulfonyl)-3-(4-bromoanilino)-acrylate 4c

Yield: 1.56 g (69 %) *after* recrystallization from ethanol, mp: 225–226 °C. IR (KBr, cm^{-1}): $\nu = 1695$ (C=O, ester); 1320, 1290 (SO_2); 1130, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.15$ (t, 3H, CH_3), 4.11 (q, 2H, O-CH_2-), 7.06 (d, 2H, 2′-H, 6′-H, J=8.9 Hz), 7.38 (d, 2H, 3′-H, 5′-H, J=8.9 Hz), 7.55 (s, 1H, 3′-H), 8.35 (s, 1H, 6′-H), 8.54 (d, 1H, vinyl CH, J=13.8 Hz), 10.71 (d, 1H, NH, J=13.8 Hz).

Anal. Calcd. for $C_{17}H_{13}BrCl_3NO_4S$: C, 39.75; H, 2.55; N, 2.73.

Found: C, 39.51; H, 2.33; N, 2.87.

Ethyl 2-(2,4,5-trichloro-phenylsulfonyl)-3-(3-methoxyanilino)-acrylate 4d

Yield: 1.30 g (62 %) *after* recrystallization from ethanol, mp: 198–199 °C. IR (KBr, cm^{-1}): $\nu = 1695$ (C=O, ester); 1320, 1290 (SO_2); 1130, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.15$ (t, 3H, CH_3), 3.82 (s, 3H, OCH_3), 4.11 (q, 2H, O-CH_2-), 6.68 (dd, 1H, 2′-H, J=1.8 Hz), 6.74–6.78 (m, 2H, 4′-H, 6′-H), 7.31 (dd, 1H, 5′-H, J=8.2 Hz), 7.55 (s, 1H, 3′-H), 8.35 (s, 1H, 6′-H), 8.58 (d, 1H, vinyl CH, J=13.9 Hz), 10.72 (d, 1H, NH, J=13.9 Hz).

Anal. Calcd. for $C_{18}H_{16}Cl_3NO_5S$: C, 46.52; H, 3.47; N, 3.01.

Found: C, 46.23; H, 3.19; N, 2.94.

Ethyl 2-(2,4,5-trichloro-phenylsulfonyl)-3-(3-chloroanilino)-acrylate 4e

Yield: 1.25 g (59 %) *after* recrystallisation from ethanol, mp: 184–185 °C. IR (KBr, cm^{-1}): ν = 1695 (C=O, ester); 1320, 1290 (SO_2); 1130, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): δ = 1.15 (t, 3H, CH_3), 4.11 (q, 2H, O-CH_2-), 6.68 (dd, 1H, 2'-H, J=1.8 Hz), 6.74–6.78 (m, 2H, 4'-H, 6'-H), 7.31 (dd, 1H, 5'-H, J=8.2 Hz), 7.55 (s, 1H, 3'-H), 8.35 (s, 1H, 6'-H), 8.58 (d, 1H, vinyl CH, J=13.9 Hz), 10.72 (d, 1H, NH, J=13.9 Hz).

Anal. Calcd. for $C_{18}H_{16}Cl_3NO_5S$: C, 43.52; H, 2.79; N, 2.99.

Found: C, 43.75; H, 2.87; N, 2.74.

Ethyl 4-(substituted-aryl)-6,7-dichloro-4H-1,4-benzothiazine 2-carboxylate-1,1-dioxide 5a-9a and ethyl 2-(2,4,5-trichloro-phenyl)-3-(N-formyl-substituted-anilino) acrylate 5b-9b

General procedure

A mixture of the corresponding acrylate **4a-e** (3.0 mmol), potassium carbonate (3.6 mmol, 1.2 eq) and silver nitrate (0.15 mmol, 5%) in DMF (30 mL) was stirred at 100°C for five hours. The reaction mixture was then allowed to stand at room temperature, filtered and the liquid filtrate poured into crushed ice, the solid obtained was filtered, washed with water, dried under vacuo, giving a mixture exclusively composed of the expected benzothiazine **5a-9a** and a desulfonated acrylate **5b-9b** which was further separated by column chromatography (hexane-ethyl acetate, 8:2).

Ethyl 4-(4-methoxyphenyl)-6,7-dichloro-4H-1,4-benzothiazine-2-carboxylate-1,1-dioxide 5a

Yield: 0.87 g (68 %), mp: 183–184 °C. IR (KBr, cm^{-1}): ν = 1700 (C=O, ester); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): δ = 1.36 (t, 3H, CH_3), 3.89 (s, 1H, OCH_3), 4.38 (q, 2H, O-CH_2-), 6.76 (s, 1H, 3-H), 7.08 (d, 2H, 2'-H, 6'-H, J=6.7 Hz), 7.26 (d, 2H, 3'-H, 5'-H, J=6.7 Hz), 7.88 (s, 1H, 5'-H), 8.17 (s, 1H, 8'-H).

Anal. Calcd. for $C_{18}H_{15}Cl_2NO_5S$: C, 50.48; H, 3.53; N, 3.27.

Found: C, 50.27; H, 3.36; N, 3.34.

Ethyl 2-(2,4,5-trichlorophenyl)-3-(N-formyl-4′-methoxyanilino) acrylate 5b

Yield: 0.29 g (23 %) mp: 108–109 °C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1620 (C=O, CHO); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.24$ (t, 3H, CH_3), 3.87 (s, 3H, OCH_3), 4.14 (q, 2H, O-CH_2-), 6.66 (d, 1H, vinyl CH, J=13.2 Hz), 6.85 (d, 2H, 2′-H, 6′-H, J=6.9 Hz), 6.95 (d, 2H, 3′-H, 5′-H, J=6.9 Hz), 7.37 (s, 1H, 6″-H), 7.62 (s, 1H, 3″-H), 7.88 (d, 1H, formyl-H, J=13.2 Hz).

Anal. Calcd. for $C_{19}H_{16}Cl_3NO_4$: C, 53.23; H, 3.76; N, 3.27.

Found: C, 53.06; H, 3.65; N, 3.32.

Ethyl 4-(4-chlorophenyl)-6,7-dichloro-4H-1,4-benzothiazine-2-carboxylate-1,1-dioxide 6a

Yield: 0.82 g (63 %), mp: 212–213 °C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.36$ (t, 3H, CH_3), 4.37 (q, 2H, O-CH_2-), 6.73 (s, 1H, 3-H), 7.33 (d, 2H, 2′-H, 6′-H, J=6.7 Hz), 7.62 (d, 2H, 3′-H, 5′-H, J=6.7 Hz), 7.85 (s, 1H, 5′-H), 8.19 (s, 1H, 8′-H).

Anal. Calcd. for $C_{17}H_{12}Cl_3NO_4S$: C, 47.19; H, 2.79; N, 3.24.

Found: C, 47.75; H, 3.03; N, 3.21.

Ethyl 2-(2,4,5-trichlorophenyl)-3-(N-formyl-4′-chloroanilino) acrylate 6b

Yield: 0.34 g (26 %) mp: 119–120 °C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1621 (C=O, CHO); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.24$ (t, 3H, CH_3), 3.87 (s, 3H, OCH_3), 4.14 (q, 2H, O-CH_2-), 6.66 (d, 1H, vinyl CH, J=13.2 Hz), 6.85 (d, 2H, 2′-H, 6′-H, J=6.9 Hz), 6.95 (d, 2H, 3′-H, 5′-H, J=6.9 Hz), 7.37 (s, 1H, 6″-H), 7.62 (s, 1H, 3″-H), 7.88 (d, 1H, formyl-H, J=13.2 Hz).

Anal. Calcd. for $C_{18}H_{13}Cl_4NO_3$: C, 49.92; H, 3.03; N, 3.23.

Found: C, 49.55; H, 3.19; N, 3.26.

Ethyl 4-(4-bromophenyl)-6,7-dichloro-4H-1,4-benzothiazine-2-carboxylate 1,1-dioxide 7a

Yield: 0.65 g (52 %), mp: 235–236°C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.35$ (t, 3H, CH_3), 4.38 (q, 2H, O-CH_2-), 6.74 (s, 1H, 3-H), 7.24 (d, 2H, 2′-H, 6′-H, J=7.0 Hz), 7.77 (d, 2H, 3′-H, 5′-H, J=7.0 Hz), 7.85 (s, 1H, 5′-H), 8.22 (s, 1H, 8′-H).

Anal. Calcd. for $C_{17}H_{12}BrCl_2NO_4S$: C, 42.72; H, 2.53; N, 2.94.

Found: C, 42.98; H, 2.47; N, 2.83.

Ethyl 2-(2,4,5-trichlorophenyl)-3-(N-formyl-4′-bromoanilino) acrylate 7b

Yield: 0.40 g (28 %), mp: 127–128 °C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1623 (C=O, CHO); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.21$ (t, 3H, CH_3), 4.13 (q, 2H, O-CH_2-), 4.65 (d, 1H, vinyl CH, J=13.3 Hz), 6.85 (d, 2H, 2′-H, 6′-H, J=6.8 Hz), 7.38 (s, 1H, 6″-H), 7.42 (d, 2H, 3′-H, 5′-H, J=6.9 Hz), 7.66 (s, 1H, 3″-H), 7.95 (d, 1H, formyl-H, J=13.3 Hz).

Anal. Calcd. for $C_{18}H_{13}BrCl_3NO_3$: C, 45.27; H, 2.74; N, 2.93.

Found: C, 45.52; H, 2.68; N, 2.87.

Ethyl 4-(3-methoxyphenyl)-6,7-dichloro-4H-1,4-benzothiazine-2-carboxylate-1,1-dioxide 8a

Yield: 0.65 g (51 %), mp: 218–219°C. IR (KBr, cm^{-1}): $\nu = 1700$ (C=O, ester); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): $\delta = 1.38$ (t, 3H, CH_3), 3.87 (s, 1H, OCH_3), 4.39 (q, 2H, O-CH_2-), 6.81 (s, 1H, 3-H), 6.85 (dd, 1H, 2′-H, J=2.2 Hz, J=2.2 Hz), 6.92 (dd, 1H, 4′-H, J=8.0 Hz, J=2.2 Hz), 7.13 (dd, 1H, 6′-H, J=8.0 Hz, J=2.2 Hz), 7.52 (dd, 1H, 6′-H, J=8.0 Hz, J=8.0 Hz), 7.92 (s, 1H, 5′-H), 8.21 (s, 1H, 8′-H).

Anal. Calcd. for $C_{18}H_{15}Cl_2NO_5S$: C, 50.48; H, 3.53; N, 3.27.

Found: C, 50.76; H, 3.21; N, 3.36.

Ethyl 2-(2,4,5-trichlorophenyl)-3-(N-formyl-3′-methoxyanilino) acrylate 8b

Yield: 0.24 g (19 %), oily residue. IR (KBr, cm^{-1}): ν = 1700 (C=O, ester); 1618 (C=O, CHO); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): δ = 1.24 (t, 3H, CH_3), 3.87 (s, 3H, OCH_3), 4.14 (q, 2H, O-CH_2-), 6.66 (d, 1H, vinyl CH, J=13.2 Hz), 6.85 (d, 2H, 2′-H, 6′-H, J=6.9 Hz), 6.95 (d, 2H, 3′-H, 5′-H, J=6.9 Hz), 7.37 (s, 1H, 6″-H), 7.62 (s, 1H, 3″-H), 7.88 (d, 1H, formyl-H, J=13.2 Hz).

Anal. Calcd. for $C_{19}H_{16}Cl_3NO_4$: C, 53.23; H, 3.76; N, 3.27.

Found: C, 53.06; H, 3.65; N, 3.32.

Ethyl 4-(3-chlorophenyl)-6,7-dichloro-4H-1,4-benzothiazine-2-carboxylate-1,1-dioxide 9a

Yield: 0.61 g (47 %), mp: 200–201 °C. IR (KBr, cm^{-1}): ν =1700 (C=O, ester); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): δ = 1.38 (t, 3H, CH_3), 4.39 (q, 2H, O-CH_2-), 6.81 (s, 1H, 3-H), 6.85 (dd, 1H, 2′-H, J=2.2 Hz, J=2.2 Hz), 6.92 (dd, 1H, 4′-H, J=8.0 Hz, J=2.2 Hz), 7.13 (dd, 1H, 6′-H, J=8.0 Hz, J=2.2 Hz), 7.52 (dd, 1H, 6′-H, J=8.0 Hz, J=8.0 Hz), 7.92 (s, 1H, 5′-H), 8.21 (s, 1H, 8′-H).

Anal. Calcd. for $C_{17}H_{12}Cl_3NO_4S$: C, 47.19; H, 2.79; N, 3.24.

Found: C, 47.32; H, 2.60; N, 3.12.

Ethyl 2-(2,4,5-trichlorophenyl)-3-(N-formyl-3′-chloroanilino) acrylate 9b

Yield: 0.27 g (21 %), mp: 72–73 °C. IR (KBr, cm^{-1}): ν = 1700 (C=O, ester); 1624 (C=O, CHO); 1330, 1300 (SO_2); 1145, 1080 (SO_2). ^1H NMR ($CDCl_3$/TMS): δ = 1.24 (t, 3H, CH_3), 3.87 (s, 3H, OCH_3), 4.14 (q, 2H, O-CH_2-), 6.66 (d, 1H, vinyl CH, J=13.2 Hz), 6.85 (d, 2H, 2′-H, 6′-H, J=6.9 Hz), 6.95 (d, 2H, 3′-H, 5′-H, J=6.9 Hz), 7.37 (s, 1H, 6″-H), 7.62 (s, 1H, 3″-H), 7.88 (d, 1H, formyl-H, J=13.2 Hz).

Anal. Calcd. for $C_{18}H_{13}Cl_4NO_3$: C, 49.92; H, 3.03; N, 3.23.

Found: C, 49.67; H, 3.15; N, 3.28.

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