$MgSO_4$, and concentrated, and the residue was distilled *in vacuo* to afford **4a** (3.2 g, 56.8 %) with b.p. 150—151 °C (2 Torr), n_D^{20} 1.5271, d_4^{20} 1.2583. Found (%): C, 65.5; H, 6.30; Cl, 14.91. $C_{13}H_{15}ClO_2$. Calculated (%): C, 65.14; H, 6.29; Cl, 14.88. ^{1}H NMR, δ: 1.58 (m, 2 H, CCH_2C); 1.70 (s, 3 H, Me); 2.04 (t, 2 H, CH_2CO); 3.51 (t, 2 H, CH_2Cl); 4.60 and 5.10 (m, 2 H, CH_2=); 6.51 (br.s, 1 H, OH); 6.94 (m, 3 H, C_6H_3).

2-(γ-Chlorobutyroyl)-6-propylphenol (4b) was synthesized similarly in 50 % yield, b.p. 176—180 °C (1.5 Torr), n_D^{20} 1.5047, d_4^{20} 1.0878. Found (%): C, 65.61; H, 6.32; Cl, 14.96. $C_{13}H_{17}ClO_2$. Calculated (%): C, 65.41; H, 6.29; Cl, 14.88.

2-(γ-Chlorobutyroyl)-6-(3-propylthiopropyl)phenol (4c) was synthesized similarly in 31.9 % yield, b.p. 208—210 °C (1.5 Torr), n_D^{20} 1.5290, d_4^{20} 1.1100. Found (%): C, 60.97; H, 7.04; Cl, 11.16; S, 9.89. $C_{16}H_{22}ClO_2S$. Calculated (%): C, 61.05; H, 7.31; Cl, 11.29; S, 10.17. ^{1}H NMR, δ: 0.88 (t, 3 H, Me); 1.43 (m, 2 H, $\underline{CH_2}Me$); 1.58 (m, 2 H, $CH_2\underline{CH_2}CH_2$); 1.76 (m, 2 H, $CH_2\underline{CH_2}CH_2$); 2.04 (t, 2 H, CH_2CO); 2.34 (t, 4 H, CH_2SCH_2); 2.66 (t, 2 H, CH_2Ar); 3.51 (t, 2 H, CH_2Cl); 6.51 (br.s, 1 H, OH); 6.94 (m, 3 H, C_6H_3).

2-(γ-Chlorobutyroyl)-4-(1-methyl-2-propylthioethyl)phenol (4d) was synthesized similarly in 46 % yield, b.p. 180—183 °C (4 Torr), n_D^{20} 1.5401, d_4^{20} 1.1354. Found (%): C, 56.27; H, 8.17; Cl, 13.01; S, 11.54. $C_{16}H_{23}ClO_2S$. Calculated (%): C, 56.01; H, 8.26; Cl, 12.75; S, 11.49. ^{1}H NMR, δ: 0.84 (t, 3 H, Me); 1.16 (q, 3 H, Me); 1.43 (m, 2 H, $\underline{CH_2}Me$); 1.90 (m, 2 H, CCH_2C); 2.04 (t, 2 H, CH_2CO); 2.34 (t, 4 H, CH_2SCH_2); 2.68 (m, 1 H, CH); 3.51 (t, 2 H, CH_2Cl); 6.51 (br.s, 1 H, OH); 6.94 (m, 3 H, C_6H_3).

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Reaction of phenoxazine and phenothiazine with 1,1-dicyano-2-(trifluoromethyl)ethylenes

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1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene alkylates phenoxazine and phenothiazine at 20 °C at the *para*-position relative to the N atom.

Key words: phenoxazine, phenothiazine, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, methyl 3,3-dicyano-2-(trifluoromethyl)acrylate, *C*-alkylation.

Reactions of phenoxazine and phenothiazine with tetracyanoethylene in DMF at 100 °C give the products of tricyanovinylation at the *para*-position relative to the N atom as a result of abstraction of HCN from the initially formed *C*-alkylation products.[1]

It is known that 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (**1**) and esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid can *C*-alkylate electron-donor aromatic and heteroaromatic compounds under mild conditions.[2]

In the present work, the reactions of phenoxazine and phenothiazine with dicyanoethylene **1** and methyl 3,3-dicyano-2-(trifluoromethyl)acrylate (**2**) were studied.

Phenoxazine and phenothiazine appeared to undergo *C*-alkylation by dicyanoethylene **1** already at 20 °C. In

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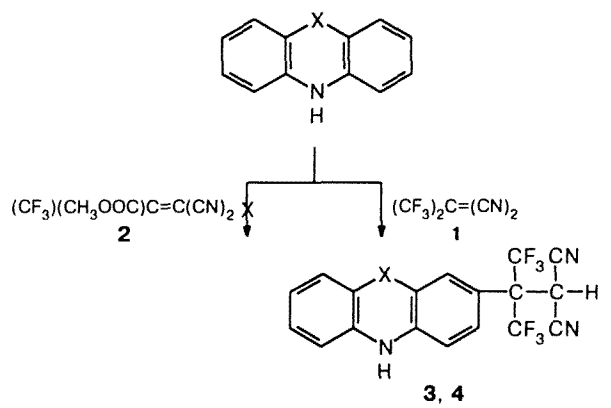
the case of phenoxazine, the reaction goes to completion in 48 h, and the 3-[2,2-dicyano-1,1-bis(trifluoromethyl)ethyl]phenoxazine (**3**) formed was isolated in 81 % yield. Phenothiazine reacts much more slowly and less distinctly. Thus, after 2 months we succeeded in the isolation of 3-[2,2-dicyano-1,1-bis(trifluoromethyl)ethyl]phenothiazine (**4**) in 22 % yield (Scheme 1).

Scheme 1



X = O (**3**), S (**4**)

According to the literature data,[1] one can assume that the side processes are associated with transformations of ion-radicals formed owing to the electron transfer in the system "electrophilic alkene—heterocycle".

Alkene **2** gives a complex mixture of products with phenoxazine. Phenothiazine under the same conditions does not react with alkene **2** at an appreciable rate; however, when heated, it also forms a complex mixture of products. Thus, it is obvious that reactions of phenoxazine and phenothiazine with alkene **2** have no practical importance. This result is in agreement with the reduced activity of alkene **2** in reactions of *C*-alkylation of aromatic compounds as compared with dicyanoethylene **1**.[2]

The structures of products **3** and **4** were established on the basis of ^1H, ^{13}C, and ^{19}F NMR spectral data.

Experimental

NMR spectra were recorded in acetone-d_6 at 20 °C on Bruker-200 SY (^{13}C, 50.31 MHz) and Bruker-AC-200F spectrometers (^1H, 200.00, and ^{19}F, 188.31 MHz, respectively). The chemical shifts of ^1H and ^{13}C were measured relative to $SiMe_4$ (internal standard) and ^{19}F relative to CF_3COOH (external standard). R_f values for compounds **3** and **4** are given for TLC on Silufol UV_{254} (Kavalier) plates.

3-[2,2-Dicyano-1,1-bis(trifluoromethyl)ethyl]phenoxazine (3). Alkene **1** (1.07 g, 5 mmol) was added to a solution of 0.91 g (5 mmol) of phenoxazine in 6 mL of $CHCl_3$ with stirring, and the mixture was kept for 48 h at 20 °C. The precipitate was filtered off and recrystallized from $CHCl_3$. Compound **3** (1.6 g, 81 %) was obtained, m.p. 171—172 °C, R_f 0.5 (CCl_4—acetone, 3:1). Found (%): C, 53.70; H, 1.94; N, 10.43. $C_{18}H_9F_6N_3O$. Calculated (%): C, 54.41; H, 2.22; N, 10.60. ^{13}C NMR, δ: 25.59 (C<u>H</u>—CN); 60.00 (q, <u>C</u>—CF_3, $^2J_{C,F}$ = 30.0 Hz); 110.42 (2 CN); 114.58, 114.63, 114.90, 114.96, 122.80, 125.11, 125.21 (C-1, C-2, C-4, C-6, C-7, C-8, C-9); 116.74 (C-3); 124.35 (q, CF_3, $J_{C,F}$ = 283 Hz); 131.86, 136.60 (C-9a, C-10a); 143.93, 145.02 (C-4a, C-5a).

3-[2,2-Dicyano-1,1-bis(trifluoromethyl)ethyl]phenothiazine (4). Alkene **1** (2.2 g, 10 mmol) was added to a solution of 2.0 g (10 mmol) of phenothiazine in 20 mL of $CHCl_3$, and the mixture was kept for 2 months at 20 °C. The crystals precipitated were filtered off and recrystallized from a hexane—$CHCl_3$ (3 : 1) mixture. Compound **4** (0.9 g, 22 %) was obtained, m.p. 169—170 °C. R_f 0.12 (CCl_4—acetone, 10 : 1). Found (%): C, 52.45; H, 2.20; N, 10.09. $C_{18}H_9F_6N_3S$. Calculated (%): C, 52.30; H, 2.18; N, 10.17. ^1H NMR, δ: 6.5 (s, 1 H, $CH(CN)_2$); 6.70—7.10 (m, 5 H); 7.30 (m, 2 H); 8.35 (s, 1 H, NH). ^{19}F NMR, δ: −13.8 (s, 2 CF_3). ^{13}C NMR, δ: 27.69 (<u>C</u>H$(CN)_2$); 60.90 (q, <u>C</u>$(CF_3)_2$, $^2J_{C,F}$ = 30 Hz); 110.55 (2 CN); 116.03, 116.27, 124.30, 126.51, 127.63, 128.78, 129.14 (C-1, C-2, C-4, C-6, C-7, C-8, C-9); 117.46 and 120.65 (C-9a, C-10a); 118.77 (C-3); 123.95 (q, CF_3, $J_{C,F}$ = 283 Hz); 141.99 and 146.17 (C-4a, C-5a).

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