and XE-60. $^1H$ and $^{19}F$ NMR spectra were recorded on a Bruker CXP-200 spectrometer relative to $SiMe_4$ and $CF_3COOH$, respectively.

**General procedure.** A solution of difluoride **1a—d** ($4 \cdot 10^{-4}$ mol) in dry $CH_2Cl_2$ (4—5 mL) was mixed with thoroughly dried KF ($1 \cdot 10^{-4}$ mol) and 18-crown-6 ($1 \cdot 10^{-4}$ mol). Then acetylene **2** ($8 \cdot 10^{-4}$ mol) was added dropwise with stirring and cooling with ice water. The mixture was stirred for 0.5 h at ~20 °C and analyzed by GLC. In all cases, only trace amounts of the initial acetylene **2** were observed in the reaction mixture, which indicates that the reaction was quantitatively. If necessary, the products were isolated by column chromatography (**5a,b**) on $SiO_2$ or by preparative GLC.

Products **4** [6] and **6** [7] were synthesized by the known procedures. **5a**. $^1H$ NMR, δ: 7.46 (m). $^{19}F$ NMR, δ: −2.56 (m, 3 F); −20.5 (m, 2 F); −49.3 (m, 2 F). **5b**. $^1H$ NMR, δ: 7.42 (m, 2 H); 7.58 (m, 3 H). $^{19}F$ NMR, δ: −59.1 (m, 2 F); −76.1 (m, 1 F); −84.6 (m, 2 F).

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# Acylation of phenols with γ-chlorobutyroyl chloride and transformations of the reaction products

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Alkylphenols afford only *O*-acyl derivatives on treatment with γ-chlorobutyroyl chloride in the presence of both $Et_3N$ and $AlCl_3$ at 20—60 °C. They cyclize under the action of $K_2CO_3$ in DMSO into the respective cyclopropanes and undergo Fries rearrangement on heating with $AlCl_3$ at 120 °C into *C*-acyl derivatives.

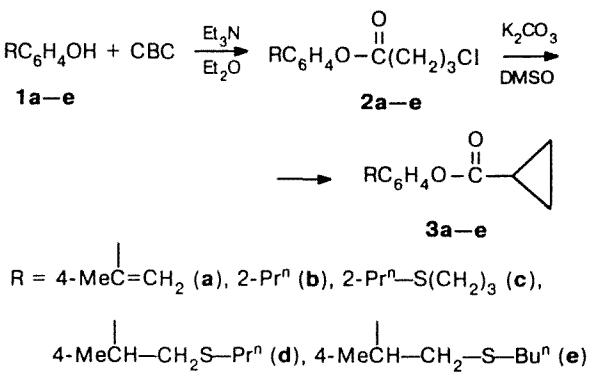
**Key words**: alkylphenols, γ-chlorobutyroyl chloride, *O*-acylation, cyclopropanes, Fries rearrangement.

Phenol has previously been shown to undergo *O*-acylation on treatment with γ-chlorobutyroyl chloride (CBC) in the presence of $Et_3N$. Under Friedel—Crafts conditions (in the presence of $AlCl_3$), only 4-acyl derivatives are formed from alkoxybenzene and only 2-acyl derivatives are formed from 4-substituted alkoxybenzenes (4-OR, Br).[1] Some reactions of these compounds have been studied.[2]

In the present work, the *O*-acylation of phenols (**1a—e**)[3—6] on treatment with CBC in the presence of $Et_3N$ and subsequent cyclization into cyclopropanes are carried out (Scheme 1).

Compounds **2d,e** were also synthesized by the thiylation of *O*-acyl derivative **2a** in the presence of azobis-

**Scheme 1**

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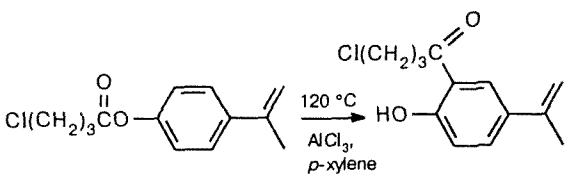
isobutyronitrile (AIBN). This reaction proceeds faster and in higher yield (90 % in 3.5 h at 80 °C) in comparison with the thiylation of original phenol **1a** (70 % in 25 h at 80 °C).[4]

The interaction of phenol **1d** with CBC under Friedel—Crafts conditions (in the presence of $AlCl_3$ at 20—60 °C) results only in the product of *O*-acylation **2d** in 20—30 % yield.

The products of *C*-acylation **4a—d** could be obtained as a result of Fries rearrangement in 32—57 % yields on heating ethers **2a—d** with $AlCl_3$ in *p*-xylene (3 h at 120 °C) according to Scheme 2 exemplified with product **4a**.

**Scheme 2**




**2a** **4a**

The structure of new compounds was confirmed by $^1H$ NMR spectroscopy. Elemental analysis data are consistent with the proposed structures.

Polyfunctional phenols **4a—d** are of interest as new synthones for heterocycles.

## Experimental

$^1H$ NMR spectra were recorded in $CCl_4$ on a Tesla BS-487C (80 MHz) spectrometer. Starting phenols **1a—e** were prepared according to the known procedures.[3—6]

***O*-(γ-Chlorobutyroyl)-4-isopropenylphenol (2a).** CBC (14 g, 0.1 mol) was added dropwise to a mixture of 4-isopropenylphenol (13.4 g, 0.1 mol) and $Et_3N$ (10.1 g, 0.1 mol) in ether (60 mL) with stirring and cooling (−10 °C) over 1 h. The mixture was stirred for an additional 2 h, the precipitate was filtered off, and the solution was washed successively with alkali and water and dried with $CaCl_2$. Then ether was evaporated, and the residue was distilled *in vacuo* to give product **2a** (16.4 g, 70 %) with b.p. 150 °C (1 Torr), $n_D^{20}$ 1.5368, $d_4^{20}$ 1.0997. Calculated (%): C, 65.41; H, 6.29; Cl, 14.88. $C_{13}H_{15}ClO_2$. Found (%): C, 65.51; H, 6.34; Cl, 14.91. $^1H$ NMR, δ: 1.95 (m, 2 H, $CCH_2C$); 2.00 (s, 3 H, Me); 2.52 (t, 2 H, $CH_2CO$); 3.42 (t, 2 H, $CH_2Cl$); 4.50 and 5.12 (m, 2 H, $CH_2$=); 6.66 and 6.99 (m, 4 H, $C_6H_4$).

***O*-(γ-Chlorobutyroyl)-2-propylphenol (2b)** was synthesized similarly in 76 % yield, b.p. 228 °C (2 Torr), $n_D^{20}$ 1.5411, $d_4^{20}$ 1.1124. Found (%): C, 67.71; H, 7.21; Cl, 13.52. $C_{13}H_{17}ClO_2$. Calculated (%): C, 67.54; H, 7.13; Cl, 13.32.

***O*-(γ-Chlorobutyroyl)-2-(3-propylthiopropyl)phenol (2c)** was synthesized similarly in 45.5 % yield, b.p. 205—208 °C (2 Torr), $n_D^{20}$ 1.5240, $d_4^{20}$ 1.11398. Found (%): C, 60.98; H, 7.04; Cl, 11.17; S, 9.88. $C_{16}H_{23}ClO_2S$. Calculated (%): C, 61.05; H, 7.31; Cl, 11.29; S, 10.17. $^1H$ NMR, δ: 0.88 (t, 3 H, Me—$CH_2$); 1.47 (m, 2 H, $CH_2$—Me); 1.60 (m, 2 H, $CH_2$—$CH_2$—Ar); 1.75 (m, 2 H, $CH_2$—$CH_2$—Cl); 2.05 (t, 2 H, $CH_2CO$); 2.35 (t, 4 H, $CH_2SCH_2$); 2.64 (m, 2 H, $CH_2Ar$); 3.51 (t, 2 H, $CH_2Cl$); 6.98 (m, 4 H, $C_6H_4$).

***O*-(γ-Chlorobutyroyl)-4-(1-methyl-2-propylthioethyl)phenol (2d)** was synthesized similarly in 69.5 % yield, b.p. 190—192 °C (3 Torr), $n_D^{20}$ 1.5315, $d_4^{20}$ 1.1322. Found (%): C, 61.27; H, 7.51; Cl, 11.12; S, 10.23. $C_{16}H_{23}ClO_2S$. Calculated (%): C, 61.05; H, 7.31; Cl, 11.29; S, 10.17. $^1H$ NMR, δ: 0.84 (t, 3 H, Me); 1.16 (d, 3 H, Me); 1.34 (m, 2 H, $CH_2$Me); 1.89 (m, 2 H, $CH_2CH_2Cl$); 2.30 (d, 2 H, $SCH_2CH$); 2.54 (t, 2 H, $CH_2CO$); 2.63 (t, 2 H, $CH_2S$); 2.63 (m, 1 H, CH); 3.40 (t, 2 H, $CH_2Cl$); 7.00 (m, 4 H, $C_6H_4$).

***O*-(γ-Chlorobutyroyl)-4-(2-butylthio-1-methylethyl)phenol (2e)** was synthesized similarly in 65.0 % yield, b.p. 195—198 °C (2 Torr), $n_D^{20}$ 1.5285, $d_4^{20}$ 1.0752. Found (%): C, 62.31; H, 7.72; Cl, 10.97; S, 9.64. $C_{17}H_{25}ClO_2S$. Calculated (%): C, 62.10; H, 7.61; Cl, 10.80; S, 9.74. $^1H$ NMR, δ: 0.88 (t, 3 H, Me); 1.16 (d, 3 H, Me); 1.43 (m, 2 H, $CH_2$Me); 1.58 (m, 2 H, $CH_2CH_2S$); 1.89 (m, 2 H, $CH_2CH_2Cl$); 2.30 (d, 2 H, $CH_2S$); 2.54 (t, 2 H, $CH_2CO$); 2.63 (t, 2 H, $CH_2S$); 2.68 (m, 1 H, CH); 3.40 (t, 2 H, $CH_2Cl$).

***O*-Cyclopropylcarbonyl-4-isopropenylphenol (3a).** A mixture of ester **2a** (2.7 g, 11 mmol) and $K_2CO_3$ (1.57 g, 11 mmol) in DMSO (40 mL) was stirred for 2 h at 60—70 °C. The mixture was cooled, water (100 mL) was added, and the product was extracted with ether. The extract was dried with $CaCl_2$, and after evaporation of ether, the residue was distilled *in vacuo* to give product **3a** (2.0 g, 87 %), b.p. 120 °C (0.2 Torr), $n_D^{20}$ 1.5470, $d_4^{20}$ 1.5470. Found (%): C, 77.18; H, 6.95. $C_{13}H_{14}O_2$. Calculated (%): C, 77.23; H, 6.93. $^1H$ NMR, δ: 0.44 and 0.72 (m, 4 H, 2 $CH_2$ of the cycle); 1.58 (m, 1 H, CH); 2.00 (s, 3 H, Me); 4.49 and 5.14 (m, 2 H, =$CH_2$); 6.66 and 6.99 (m, 4 H, $C_6H_4$).

***O*-Cyclopropylcarbonyl-2-propylphenol (3b)** was synthesized similarly in 82.6 % yield, b.p. 147—150 °C (4 Torr), $n_D^{20}$ 1.5311, $d_4^{20}$ 1.09714. Found (%): C, 76.39; H, 7.69. $C_{13}H_{16}O_2$. Calculated (%): C, 76.47; H, 7.84.

***O*-Cyclopropylcarbonyl-2-(3-propylthiopropyl)phenol (3c)** was synthesized similarly in 64.95 % yield, b.p. 177—180 °C (4 Torr), $n_D^{20}$ 1.5250, $d_4^{20}$ 1.09205. Found (%): C, 68.87; H, 7.64; S, 11.03. $C_{16}H_{22}O_2S$. Calculated (%): C, 69.06; H, 7.91; S, 11.51. $^1H$ NMR, δ: 0.44 and 0.72 (m, 4 H, 2 $CH_2$ of the cycle); 0.87 (t, 3 H, Me); 1.47 (m, 2 H, $CH_2$Me); 1.58 (m, 1 H, CH); 1.74 (m, 4 H, $CH_2CH_2CH_2$); 2.39 (t, 4 H, $CH_2SCH_2$); 2.61 (t, 2 H, $CH_2Ar$); 6.91 (m, 4 H, $C_6H_4$).

***O*-Cyclopropylcarbonyl-4-(1-methyl-2-propylthioethyl)phenol (3d)** was synthesized similarly in 84.7 % yield, b.p. 160—165 °C (1 Torr), $n_D^{20}$ 1.5420, $d_4^{20}$ 1.1322. Found (%): C, 69.21; H, 8.02; S, 11.70. $C_{16}H_{22}O_2S$. Calculated (%): C, 69.06; H, 7.91; S, 11.51. $^1H$ NMR, δ: 0.44 and 0.72 (m, 4 H, 2 $CH_2$ of the cycle); 0.85 (t, 3 H, Me); 1.16 (d, 3 H, MeCH); 1.40 (m, 2 H, $CH_2$Me); 1.58 (m, 1 H, CH); 2.3 (d, 2 H, $CH_2S$); 2.63 (t, 2 H, $SCH_2$); 2.68 (m, 1 H, CH); 6.70 and 7.00 (m, 4 H, $C_6H_4$).

***O*-Cyclopropylcarbonyl-4-(2-butylthio-1-methylethyl)phenol (3e)** was synthesized similarly in 75.5 % yield, b.p. 180—183 °C (4 Torr), $n_D^{20}$ 1.5428, $d_4^{20}$ 1.0817. Found (%): C, 69.88; H, 8.19; S, 10.97. $C_{17}H_{24}O_2S$. Calculated (%): C, 69.82; H, 8.22; S, 10.96.

**2-(γ-Chlorobutyroyl)-4-isopropenylphenol (4a).** A mixture of compound **2a** (0.1 mol) and $AlCl_3$ (0.1 mol) in *p*-xylene (200 mL) was stirred for 3 h at 120 °C in an argon atmosphere. After cooling, the mixture was poured into a solution of conc. HCl (20 mL) in water (800 mL). The organic layer was separated and washed with water to pH 7, dried with

$MgSO_4$, 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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