pentene (320 mg, 1.5 mmol) was added at −70 °C, and the mixture was stored for 2 h. The temperature of the reaction mixture was brought to room temperature, 2 mL of water and a solution of 0.1 mL of concentrated HCl in 1 mL of water were added. The solvents were removed *in vacuo*, and the residue was dissolved in $CHCl_3$, washed with water, and dried with $CaCl_2$. $CHCl_3$ was removed, and the product was isolated by preparative TLC using $CHCl_3$ as the eluent. Compound **5** (200 mg, 49%) with m.p. 122—124 °C was obtained. ^{1}H NMR ($DMSO$-d_6), δ: 2.59 (s, 3 H, CH_3); 7.39—7.48 (m, 2 H, H(5), H(6)); 7.73—7.81 (m, 2 H, H(4), H(7)); 7.91 (s, 1 H, H(4′)). ^{19}F NMR ($CDCl_3$), δ: −128.1 (s, 2 F, CF_2); −124.5 (s, F, CF); −116.2 (s, 2 F, CF_2); −106.7 (s, 2 F, CF_2). MS, *m/z* (I_{rel} (%)): 407 $[M]^+$ (100%).

1,2-Bis[2-methyl-5-(benzoxazol-2-yl)thien-3-yl]hexafluorocyclopentene (1). A 1.75 *N* solution (0.32 mL) of Bu^nLi (0.56 mmol) in ether was added to a solution of compound **2** (150 mg, 0.51 mmol) in THF (4 mL) with stirring at −70 °C (Ar), and the mixture was kept for 10 min. Then a solution of compound **5** (200 mg, 0.49 mmol) in THF (2 mL) was added at −70 °C, and the mixture was stored for 2 h. The temperature of the reaction mixture was brought to room temperature, and the solution was left to stand for ~12 h. Water (5 mL) and concentrated HCl (0.1 mL) were added. The solvents were removed *in vacuo*, and the residue was dissolved in $CHCl_3$, washed with water, a 5% solution of Na_2CO_3, and again with water, and dried above $CaCl_2$. $CHCl_3$ was removed. The product was isolated on a chromatographic column (Silpearl, benzene as the eluent). Compound **1** (92 mg, 31%), with m.p. 194—195 °C was obtained. Found (%): C, 57.26; H, 2.95. $C_{29}H_{16}F_6N_2O_2S_2$. Calculated (%): C, 57.80; H, 2.67. ^{1}H NMR ($CDCl_3$), δ, 1A (open form): 2.06 (s, 3 H, CH_3); 7.30—7.42 (m, 2 H, H(5), H(6)); 7.5—7.6 (m, 1 H, H(4)); 7.7—7.8 (m, 1 H, H(7)); 7.92 (s, 1 H, H(4′)); 1B (cyclic form): 2.32 (s, 3 H, CH_3); 5.30 (s, 1 H, H(4′)). ^{19}F NMR ($CDCl_3$), δ: −131.5 (s, 2 F, CF_2); −110 (s, 4 F, $(CF_2)_2$). MS, *m/z* (I_{rel} (%)): 602 $[M]^+$ (60%).

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High-pressure alkylation of azomethines
1. Synthesis of *N*-monoalkylanilines

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Reaction of anils with alkyl halides under high pressure (10 kbar) was studied. Alkylation in polar media (dioxane or acetonitrile) followed by hydrolysis yields pure *N*-monoalkylanilines in high yields. Optimum conditions for high-pressure alkylation were found.

Key words: azomethines, alkylation, immonium salts, *N*-monoalkylanilines, high pressure.

It is well known that direct alkylation of primary amines yields mixtures of products that are difficult to separate, pure dialkylamines being especially hard to isolate. Pure *N*-monoalkylanilines can be obtained in various ways,[1] including alkylation of easily available azomethines followed by hydrolysis of the resulting quaternary immonium salts.[2]

This method is quite promising, but it works well only with active alkylating agents, probably, because of the low nucleophilicity of azomethines. Even when highly

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Table 1. Yields of *N*-monoalkylanilines **4—13***

Azomethine	R	Alkyl halide	Product	R, R′	Yield (%)	$[M]^+$, *m/z*
1a	H	EtCl (**2a**)	**4**	H, Et	82	121
1a	H	EtBr (**2b**)	**4**	H, Et	91	121
1a	H	Pr^nCl (**2c**)	**5**	H, Pr^n	83	135
1a	H	Bu^nCl (**2d**)	**6**	H, Bu^n	80	149
1b	Cl	Pr^nCl (**2c**)	**7**	Cl, Pr^n	76	170
1b	Cl	Bu^nCl (**2d**)	**8**	Cl, Bu^n	73	184
1c	Br	Pr^nCl (**2c**)	**9**	Br, Pr^n	75	214
1d	Me	Pr^nCl (**2c**)	**10**	Me, Pr^n	85	149
1d	Me	Bu^nCl (**2d**)	**11**	Me, Bu^n	86	163
1e	MeO	Pr^nCl (**2c**)	**12**	MeO, Pr^n	88	165
1e	MeO	Bu^nCl (**2d**)	**13**	MeO, Bu^n	89	179

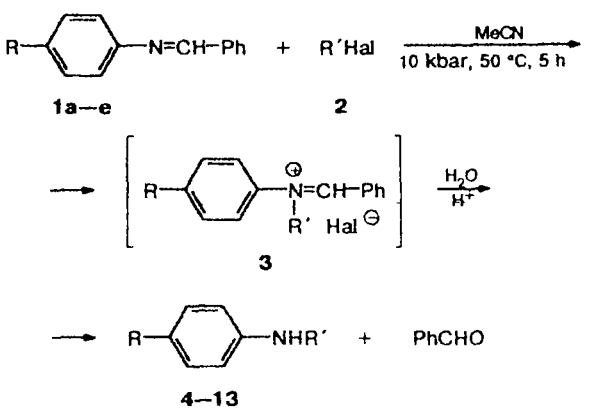
* The yields were determined from the GLC data after hydrolysis of the reaction mixture.

reactive alkyl halides are used, the reaction mixture should be kept at high temperatures for a long period of time, which leads to resinification and hence to a decrease in the yields of *N*-monoalkylanilines.[3]

It is known that high pressure significantly accelerates the formation of quaternary ammonium salts.[4,5] That is why one could expect the same effect in the case of quaternary immonium salts obtained from Schiff bases, which is not described in the literature so far.

Azomethines **1a—e** synthesized from benzaldehyde and *para*-substituted anilines bearing either donor (Me or MeO) or acceptor (Cl or Br) substituents were the subject of our investigation. We found the conditions under which azomethines **1** are smoothly alkylated at a pressure of 10 kbar (Scheme 1, Table 1) not only by alkyl bromides (**2**, Hal = Br), but also by less active alkyl chlorides (**2**, Hal = Cl). The initial anilines were not detected in the reaction products after decomposition of the corresponding salts.

Scheme 1



It turned out that the yields of *N*-alkylanilines depend on the electronic properties of anil. For example, the presence of electron-releasing substituents (compounds **1d,e**) increases, while the presence of electron-withdrawing substituents (compounds **1b,c**) decreases, their yields (see Table 1), which can be explained by a higher nucleophilicity of azomethines containing donor groups.

Table 2. The dependence of the yield of *N*-propyl aniline (**5**)* on the reaction conditions

Run	Solvent	*T*/°C	*p*/kbar	*t*/h	Yield of **5** (%)
1	PhMe	50	10	1	47**
2	PhMe	50	10	5	52**
3	Dioxane	50	10	5	62
4	MeCN	50	10	5	83
5	MeCN	20	10	5	60
6	MeCN	85	10	5	76
7	MeCN	50	5	5	67

* The yields were determined from the GLC data after hydrolysis of the reaction mixture.
** Aniline (~20—30%) was detected in the reaction mixture.

The reaction of benzalaniline with propyl chloride was used to find the optimum reaction conditions (Table 2). Our experiments showed that alkylation in quite polar media such as dioxane or acetonitrile proceeds to completion, and hydrolysis of the reaction mixtures gives *N*-monoalkylanilines in high yields. In solvents of low polarity such as toluene, the yield of alkylated aniline is lower, and the reaction products contain considerable amounts of the unreacted aniline (see Table 2, runs *1* and *2*). Extension of the reaction time from one to five hours proved to increase slightly the yield of monoalkylaniline. The optimum reaction temperature was found to be ~50 °C. The reaction at higher temperatures is accompanied by marked resinification (see Table 2, run *6*), while that at lower temperatures (20 °C) gives much lower yields (see Table 2, run *5*). It was also found that, when pressure was reduced to 5 kbar (see Table 2, run *7*), the yield was somewhat decreased.

Thus, the optimum reaction conditions are alkylation of azomethines in acetonitrile at 10 kbar and 50 °C for 5 h, which gives *N*-monoalkylanilines in overall 73—91% yields after hydrolysis of the intermediate salt.

Experimental

Melting points were measured on a Boetius hot stage. GLC-MS analysis was performed on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, a capillary column 30 m × 0.25 mm with polydimethylsiloxane (0.25 μ) as a grafted phase). Azomethines **1a—e** were synthesized according to the known procedure.[6]

Alkylation of azomethines 1a—e under high pressure (general procedure). A solution of azomethine (1 mmol) and alkyl halide (**2a—d**) (1.1 mmol) in 1 mL of MeCN was kept in a Teflon ampoule under a pressure of 10 kbar and at 50 °C for 5 h. The reaction mixture was cooled and concentrated *in vacuo*. The residue was diluted with 3 mL of 5% HCl and

refluxed for 3 min. On cooling, the benzaldehyde was extracted with ether (2×5 mL), and the aqueous layer was alkalized with a solution of NaOH to a strong alkaline reaction. The *N*-alkylaniline that formed was extracted with ether (3×5 mL), and the extract was analyzed by GLC with hexadecane as the internal standard. Calibration was performed with known mixtures for each monoalkylaniline obtained and the standard.

***N*-Butylaniline (6).** The reaction was carried out with the use of benzalaniline (**1a**) and *n*-butyl chloride (**2d**) according to the above procedure, except that the ethereal solution of *N*-butylaniline was dried with anhydrous K_2CO_3 and treated with dry HCl. The *N*-butylaniline hydrochloride that formed was recrystallized from ethyl acetate. Yield 76%, m.p. 114—115 °C (*cf.* Ref. 7: m.p. 115 °C).

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Seasonal dynamics of distribution of isoprenologs of bound polyprenols and dolichols in leaves and branches of *Alnus glutinosa* (L.) Gartn.

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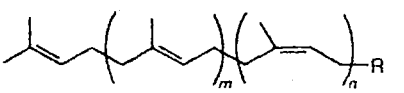
Polyisoprenoid alcohols (polyprenols and dolichols) from leaves and branches of European alder (*Alnus glutinosa* (L.) Gartn.) were studied by ^{1}H NMR spectroscopy and HPLC. Data on dynamics of relative monthly (May—August) content of each isoprenolog of polyprenols and dolichols were obtained.

Key words: polyisoprenoids, polyprenols, dolichols, high performance liquid chromatography, ^{1}H NMR spectra.

Acyclic polyisoprenoids, polyprenols, are usual constituents of a set of chemical compounds found in plant cells. Polyprenyl pyrophosphates play an important physiological function in plants, participating in biosynthesis of oligosaccharides and glycoproteins.[1] 2,3-Dihydroderivatives of polyprenols (dolichols),[2—4] which are present in animal but rarely in plant organisms, attract more and more attention of researchers due to the importance of these compounds for development of living organisms.[5] Polyprenols and their derivatives are characterized by a wide spectrum of biological activity, described in the review.[6]

The molecular structures of polyprenols and dolichols, which are usually found in nature as a mixture of isoprenologs, are represented by formulas **1** and **2** respectively, where *m* is usually 2 for polyprenols of conifers and dolichols and 3 for polyprenols of deciduous plants, and *n* varies within a rather wide range.[7] In plants polyprenols occur as free alcohols, acetates,[8] or esters of higher fatty acids,[3,9] and dolichols usually occur as esters.[2—4]



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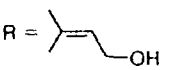
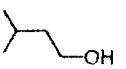
1: R = 

2: R = 

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