N,N'-Bis[2,2-di(4-hydroxyphenyl)propane]piperazine (IVc). An 8.6 g sample of piperazine and 45.6 g of diphenylolpropane in 75 ml of methanol and 40 ml of 36% aqueous formaldehyde was heated for 4 h at 70°C. The product was purified by crystallization from ether.

N,N'-Bis[2,2-di(4-hydroxyphenyl)propane]-N-(β-aminoethyl)piperazine (IVd). A mixture of 12.9 g of N-(β-aminoethyl)piperazine, 25 ml of 36% aqueous formaldehyde, and 45.6 g of diphenylpropane was heated for 10 h, initially at 40°C, and then at 90°C. The product was purified by crystallization from alcohol–ether (1:2).

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SYNTHESIS OF FLUORO-SUBSTITUTED SYMMETRICAL DIALKYLAMINOTRIAZINES UNDER INTERPHASE-CATALYSIS CONDITIONS

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The reaction of chloro derivatives of symmetrical dialkylaminotriazines with potassium fluoride in the presence of catalytic amounts of crown ethers or quaternary ammonium salts leads to the formation of the corresponding fluoro derivatives in high yields. The structure of the catalyst and the nucleophilicity of the solvent affect the yields of the fluoro derivatives of the symmetrical dialkylaminotriazines.

Fluoro-substituted symmetrical dialkylaminotriazines are promising intermediates in the synthesis of biologically active compounds and, therefore, their production is an important and urgent task.

Due to the decreased π-electron density on the carbon atoms of the heteroring, symmetrical dialkylaminotriazine are active in nucleophilic substitution reaction, the ease of which decreases with the degree to which electron-donor substituents are introduced into the triazine molecule. The reactivities of the compounds decrease in the following order: trichloro-, dichloro-, and monochlorotriazines [1].

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	NMR spectrum, δ, ppm (J, Hz)	
		^{13}C	^{19}F
V	195...196	169,4 (d, J_{CF}=211,5, 2-C); 167,7 (4-C); 166,8 (s, 6-C); 35,5 (t, J_{CH}=135,5, CH_2—CH_3); 14,86 (q, J_{CH}=125,9, CH_2—CH_3); 43,69 (d, J_{CH}=137,3, CH—$(CH_3)_2$); 22,68 (q, J_{CH}=126,5, CH—$(CH_3)_2$)	−34,1c
VI	95...96	169,2 (d, J_{CF}=209,2, 2-C); 166,4 (d, $^3J_{CF}$=8,4, 4-C); 165,6 (d, $^3J_{CF}$=8, 6-C); 46,4 (d, J_{CH}=137,9, CH—$(CH_3)_2$); 20,44 (q, J_{CH}=126,5, CH—$(CH_3)_2$); 66,39 (t, NCH_2CH_2O); 44,33 (t, NCH_2CH_2O)	−36,3
VII	252...253	169,6 (d, J_{CF}=210, 2-C); 167,3 (s, 4-C); 166,4 (s, 6-C); 44,7 (d, CH—$(CH_3)_2$); 22,64 (q, CH—$(CH_3)_2$); 66,29 (t, NCH_2CH_2O); 44,13 (t, NCH_2CH_2O)	−35,02
VIII	146...147	—	−33,7

TABLE 2. Effect of the Solvents on the Yield of 2-Fluoro-4-isopropylamin-6-ethylamino-1,3,5-triazine (1) (τ 4 h, T 140°C, dicyclohexano-18-crown-6 as catalyst)

Solvent	ε^{20} [5]	Nucleophilicity, cm^{-1} (6)	Yield, %
Dimethyl sulfone	—	—	98
Methyl ethyl sulfone	—	—	97
DMSO	48,90	362	94
DMF	36,70	291	24
Nitrobenzene	34,82	67	8
Aceteonitrile*	37,50	160	21

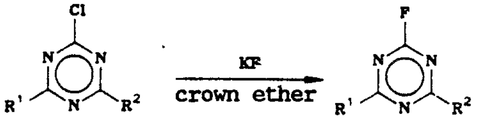
*Reaction temperature 80°C.

TABLE 3. Effect of the Catalysts on the Yield of V (τ 4 h, T 140°C, DMSO as solvent)

Catalyst	Yield, %
No catalyst	54
DCH 18-K-6	94
15-Crown-5	47
Dibenzo-24-crown-8	39
TEPDAB	66
TBAI	49

With respect to their reactivities in nucleophilic substitution reactions, symmetrical dialkylaminotriazines, in many respects, are identical to aromatic nitro compounds; this makes it possible to assume the possibility of their fluorination in analogy with the fluorination of aromatic chloro-substituted nitro compounds [2, 3].

We have studied the fluorination of 2-chloro-4,6-dialkylamino-1,3,5-triazines I-IV with anhydrous potassium fluoride. We demonstrated that fluorotriazines V-VIII are formed in 93-99% yields in the presence of a catalytic amount of dicyclohexano-18-crown-6 (Table 1):



I-IV

V-VIII

V, VII, VIII R^1=NH(i-C_3H_7), VI R^1=N(i-C_3H_7)$_2$; V R^2=NHC_2H_5, VI VII R^2 morpholino, VIII R^2=NH(i-C_3H_7)

The polarity of the solvent (Table 2) has a substantial effect on the reaction rate and the yield of the fluorinated product; the yield of the product does not correlate with the dielectric permeability but rather with the nucleophilicity of the solvent.

The catalytic effect is manifested by only two of the investigated catalysts, viz., dicyclohexano-18-crown-6 (DCH 18-K-6) and triethylpentadecylammonium bromide (TEPDAB). The low activity of 15-crown-5 and dibenzo-24-crown-8 is evidently explained by the nonconformity of the sizes of the cavity of the catalyst and the poassium ion, while the low activity of tetrabutylammonium iodide (TABAI) is evidently explained by the known poisoning effect of the iodide ion [4] (see Table 3).

EXPERIMENTAL

The NMR spectra of solutions of the compounds in DMSO were recorded with a Bruker CXP-100 spectrometer with octamethylcyclotetrasiloxane or trifluoroacetic acid as the internal standard.

Products V-VIII were analyzed by GLC with a CHROM-5 chromatograph with a flame-ionization detector and an IT2 integrator; the glass spiral column (2 m × 3 mm) was packed with Chromaton N-AW (grain size 0.25-0.315 mm) as the support, 5% PEG 40 m as the stationary phase, and nitrogen as the carrier gas. The vaporization temperature was 170°C, and the thermostat temperature of the columns was 160°C. The mass spectra were recorded with an MKh-1303 mass spectrometer with direct introduction of the samples (70 eV, 230°C).

General Method for the Synthesis of V-VIII. A reactor equipped with a thermometer, stirrer, and reflux condensor was charged with 20 ml of the corresponding solvent, 0.04 mole of the triazine, 0.08 mole of potassium fluoride, and 5% of the interphase catalyst. The reaction mixture was stirred at 140°C for 4 h, after which 100 ml of distilled water was added, and the resulting precipitate was removed by filtration, washed with distilled water, and dried.

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