CONCLUSIONS

AgBr microparticles, containing a calculated number of Ag^+ ions in the range from 6 to 20, were synthesized in the dispersed phase of water–oil microemulsions.

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SYNTHESIS OF VICINAL BROMOALKYLAMINES CONTAINING A TRIFLUOROMETHYL GROUP

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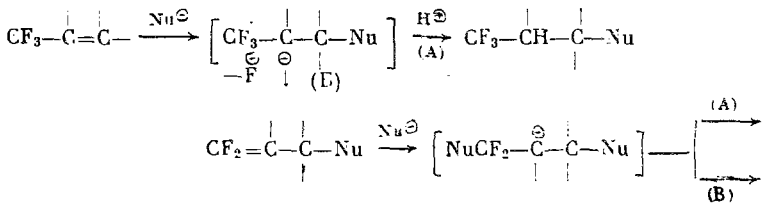
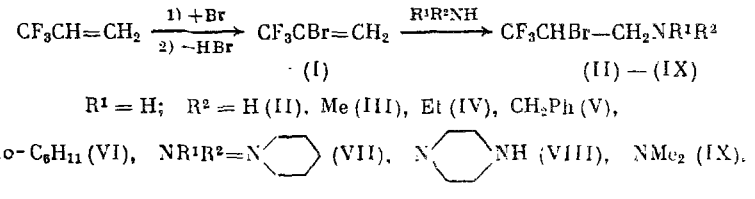
Vicinal haloamines have marked physiological activity and are key compounds in organic synthesis [1]. The modification of biologically active compounds by the introduction of fluorine or fluoroalkyl substituents leads in several cases to an enhancement of activity and more selective action [2].

In the present work, vicinal haloamines were synthesized starting from trifluoropropylene. In contrast to the data for perfluoroolefins [3], there have been only a few reports of nucleophilic substitution reactions with olefins containing a trifluoromethyl group [4, 5].

The structures of the products formed are a function of the reactivity of the intermediate carbanion, which is stabilized either by the addition of a proton (A) or elimination of a fluoride anion (B). The fluoroolefin formed upon elimination of a fluoride anion may be subjected to subsequent nucleophilic attack at the CF_2 group, leading to exhaustive elimination of fluorine and tar formation, as also observed in the reaction of MeONa with trifluoropropylene [4].



We were able to carry out the addition of a series of aliphatic amines and ammonia to 1,1,1-trifluoro-2-bromopropylene (I).



The optimal yield of adducts (II)-(VIII) is obtained upon the reaction of (I) with excess amine without solvent at 20°C for several days. Dilution of the reaction mixture by an aprotic polar solvent reduces the conversion. The reaction with ammonia is carried out in absolute sulfolane and leads to the formation of the corresponding primary amine (II). When DMF is used as the solvent, 3,3,3-trifluoro-2-bromopropyldimethylamine (IX) was isolated in-

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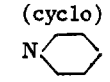
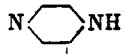
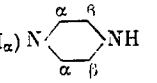
TABLE 1. Bromoalkylamines (II)-(IX), $CF_3CHBrCH_2NR^1R^2$

Compound	R^1	R^2	Reaction time, days	Yield, %	Mp, °C, bp, °C (p, mm Hg)	Found/Calculated, % C	H	F	N	Chemical formula
(II) *	H	H	1	25	45(60)	15.8 / 16.2	2.59 / 2.69	–	6.0 / 6.1	$C_3H_6BrClF_3N$
(III)	H	Me	1	46	55(60)	23.5 / 23.3	3.40 / 3.40	27.8 / 27.7	6.9 / 6.8	$C_4H_7BrF_3N$
(IV)	H	Et	3	45	35(15)	27.2 / 27.3	4.05 / 4.08	25.7 / 25.9	–	$C_5H_9BrF_3N$
(V) †	H	CH_2Ph	10	60	120(10)	32.8 / 33.0	3.33 / 3.30	15.2 / 15.7	3.9 / 3.8	$C_{10}H_{12}Br_2F_3N$
(VI)	H	C_6H_{11} (cyclo)	3	45	85(10)	39.7 / 39.5	5.40 / 5.47	–	5.2 / 5.1	$C_9H_{15}BrF_3N$
(VII)			2	85	76(15)	36.6 / 36.8	4.99 / 5.00	–	5.6 / 5.4	$C_8H_{13}BrF_3N$
(VIII)			5	40	110(5)	32.4 / 32.2	4.25 / 4.60	–	–	$C_7H_{12}BrF_3N_2$
(IX)	Me	Me	10	56	126(760)	27.4 / 27.4	4.15 / 4.09	25.5 / 25.9	–	$C_5H_9BrF_3N$

*Characterized as the hydrochloride salt, mp 232°C (from $CHCl_3$).
†Characterized as the hydrobromide salt, mp 200°C (from ethanol).

TABLE 2. NMR Spectra of $CF_3CBr{=}CH_2$(I), $CF_3CHBrCH_2NR^1R^2$ (II)-(IX)

Compound	δ, ppm >CH	>CH_2	other signals	CF_3 (J, Hz)
(I)	–	5.5m, 6.0m	–	–9.5s
(II)	4.35m	3.1d.d, 3.25d.d	1.75s (NH_2)	–7.3d
(III)	4.2m	2.7d.d, 2.8d.d	1.1br.s (NH), 2.15s (NCH_3)	–6.9d
(IV)	4.25m	2.9d, 3.0d	1.0m (CH_3), 1.2s (NH), 2.6m (CH_2)	–6.4d(7.52)
(V)	4.15	2.95d, 3.0s	1.5br.s (NH), 3.65s (CH_2Ph), 7.16m (Ph)	–7.3d(7.5)
(VI)	4.0m	2.9m	1.0–1.5m (C_6H_{11}), 2.1br.s (NH)	–7.55d(7.7)
(VII)	4.1m	2.6d, 2.75s	1.4m ($2H_\beta$, H_γ), 2.3m ($2H_\alpha$) 	–7.7d(7.52)
(VIII)	3.8m	2.5m	1.6s (NH), 2.0m ($2H_\beta$), 2.5m ($2H_\alpha$) 	–7.7d
(XI)	4.0m	2.65d, 2.75d	2.2s ($N(CH_3)_2$)	–7.0d

stead of the expected addition product. The formation of (IX) is apparently a result of a unique transamination reaction of DMF in the presence of excess liquid ammonia with the release of dimethylamine. The reaction with ammonia is not observed in nonpolar solvents, while olefin (I) is completely decomposed with the formation of NH_4F, NH_4Br, and tar in excess liquid ammonia without solvent. Analogous side products are also obtained upon the reaction of (I) with primary amines. The addition of secondary amines such as piperidine and piperazine proceeds smoothly to give bromoalkylamines (VII) and (VIII) in high yields. On the other hand, it was impossible to carry out the reaction with diethylamine under analogous conditions. This failure is probably a consequence of steric factors.

NMR spectroscopy indicates an anti-Markovnikov course for the addition of aliphatic amines to (I).

EXPERIMENTAL

The ^1H NMR spectra were taken on a Bruker WP-200SY spectrometer at 200 MHz and on a Tesla BS-467 spectrometer at 60 MHz in CCl_4 solution with HMDS as an internal standard. The

^{19}F NMR spectra were taken on a Perkin–Elmer R-32 spectrometer at 84.6 MHz with CF_3CO_2H as an external standard. The reaction conditions, yields, and characteristics for bromoalkylamines (II)-(IX) are given in Table 1. The NMR spectral data are given in Table 2.

3,3,3-Trifluoro-2-bromopropylamine (II). A mixture of 25.0 g (0.143 mole) (I) [6], 30 ml abs. sulfolane, and 15 ml liquid ammonia was added to a 250-ml glass ampul. The ampul was sealed, maintained at 20°C for 24 h, frozen, and opened. The volatile products were collected in a cold trap upon gradual warming to 50°C to give 6 ml NH_3 and 5 g unreacted (I), which was identified by NMR spectroscopy after the dissolution of NH_3 in water. Adduct (II) was distilled from the ampul in vacuo at 150 mm, redistilled at 45°C (60 mm), and characterized as the hydrochloride salt after treatment with ethanolic HCl (Table 1). The residue in the ampul (60 g) consisted of sulfolane, tarry products, and NH_4F (9 g). The latter was characterized by ^{19}F NMR spectroscopy: δ 65 ppm (s) in water.

A mixture of 35.0 g (0.2 mole) olefin (I), 26 ml (1.0 mole) liquid NH_3, and 30 ml abs. DMF in a steel ampul under analogous conditions gave 3,3,3-trifluoro-2-bromopropyldimethylamine (IX) in 56% yield.

3,3,3-Trifluoro-2-bromopropylmethylamine (III) and 3,3,3-trifluoro-2-bromopropylethylamine (IV) were obtained by analogy from 8.75 g (0.05 mole) (I) and 2.0 g (0.065 mole) methylamine and from 5.25 g (0.03 mole) (I) and 2.25 g (0.05 mole) ethylamine, respectively.

3,3,3-Trifluoro-2-bromopropylbenzylamine (V), 3,3,3-trifluoro-2-bromopropylcyclohexylamine (VI), 3,3,3-trifluoro-2-bromopropylpiperidylamine (VII), and 3,3,3-trifluoro-2-bromopropylpiperazylamine (VIII) were obtained under analogous conditions from 0.05 mole (I) and 0.06 mole of the corresponding amine. In the case of piperazine, 10 ml abs. ethanol was used as the solvent. The reaction mixture was diluted with 30 ml water and extracted with three 20-ml portions of ether. The ethereal extract was washed with 20 ml water and dried over $MgSO_4$. Ether was removed and the product was distilled in vacuum.

CONCLUSIONS

The reaction of 1,1,1-trifluoro-2-bromopropylene with ammonia and a series of aliphatic amines gave vicinal bromoalkylamines, containing a trifluoromethyl group.

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