Reactions of Trifluoromethyl Bromide and Related Halides: Part 10. Perfluoroalkylation of Aromatic Compounds induced by Sulphur Dioxide Radical Anion Precursors

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Perfluoroalkylation of electron-rich aromatic compounds with trifluoromethyl bromide, or long-chain perfluoroalkyl iodides, was performed in the presence of sodium dithionite or zinc–sulphur dioxide. This alkylation occurred at the *ortho* and *para* positions relative to the amino or hydroxy substituent. Pyrroles were perfluoroalkylated regioselectively at the 2-position. This alkylation was interpreted as a radical aromatic substitution; the formation of the perfluoroalkyl radical can be induced by a single-electron transfer from sulphur dioxide radical anion to the perfluoroalkyl halide.

An indication of the presence of an intermediate trifluoromethyl radical in the trifluoromethanesulphinate salt formation from trifluoromethyl bromide, sulphur dioxide, and zinc was the alkylation of electron-rich aromatic compounds introduced into the reaction medium.[1,2] Similar perfluoroalkylations have been observed with longer chain perfluoroalkyl iodides (preliminary communication; ref. 2) (Scheme 1, method A). The first step of this triflinate salt synthesis was interpreted by a reduction of sulphur dioxide to its corresponding radical anion[1–3] (Scheme 2). This reaction has been also performed electrochemically.[4,5] Recently, other sources of sulphur dioxide radical anion, such as sodium dithionite $S_2O_4^{2-}$, or hydroxymethanesulphinate salts, have been used for triflinate salt preparation.[6] Similarly to the zinc–sulphur dioxide procedure, ring perfluoroalkylations occurred when aromatic compounds were added to the medium (Scheme 1, method B). We compare here the results obtained by method A and method B.

$$ArH + R_FX \xrightarrow[\text{or } Na_2S_2O_4 \text{ (method B)}]{Zn/SO_2 \text{ (method A)}} ArR_F + HX$$

$R_FX = CF_3Br, CF_3[CF_2]_nI$ with $n = 0, 1, 3, 5, 7$

Scheme 1.

$$2SO_2 \longrightarrow 2\,SO_2^{\cdot-} \; (\rightleftarrows {}^-SO_2\text{–}SO_2^-)$$

$$SO_2^{\cdot-} + CF_3Br \longrightarrow SO_2 + Br^- + CF_3^{\cdot}$$

Scheme 2.

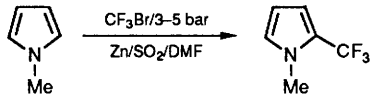
Results

Perfluoroalkylation in the Presence of Zinc and Sulphur Dioxide.—Trifluoromethylation has been performed by addition of an aromatic compound at the beginning of the triflinate salt preparation. It appeared that 0.15 mol equiv. of zinc and sulphur dioxide were sufficient to induce the alkylation of the aromatic nucleus. A base, such as sodium 'metabisulphite' ($Na_2S_2O_5$) or a pyridine derivative, was placed in the medium in order to neutralize the hydrobromic acid formed. The exothermic reaction was performed in dimethylformamide (DMF) at room temperature for 2 hours under a pressure of 3–5 bar of trifluoromethyl bromide in a Parr apparatus, with CF_3Br (~ 1.5 mol per mol of aromatic) used.

The yield and the selectivity were very dependent on the nature of the aromatic compound. From toluene, the total yield was only 22%. The three *ortho*, *meta*, *para* isomers, in the proportions 9:4:9, were separated by GLC and characterized by ^{19}F NMR analysis. In the case of aniline, the *meta*-isomer was not detected. The *ortho* and *para* isomers were separated. The total yield of purified trifluoromethylaniline was 56%. Various arylamines were similarly trifluoromethylated (Table 1). In the case of 2-chloroaniline, besides 2-chlorotrifluoromethylanilines, 2-trifluoromethylaniline was obtained. This compound can result from a further reduction by the metal or from an *ipso*-substitution.[7] Alkylation of phenols was also oriented towards the *ortho* and *para* positions, but the yield was generally lower than that with anilines (Table 1).

The more reactive liquid perfluoroalkyl iodides allowed us to perform the alkylation at atmospheric pressure. Stoicheiometric quantities of anilines and perfluorobutyl iodide were used. Analysis of the products showed the formation of equal amounts of *ortho* and *para* isomers of perfluorobutylanilines.

In some experiments with trifluoromethyl bromide, small signals were detected by ^{19}F NMR spectroscopy, which could correspond to the trifluoromethylation products of the pyridines used as base. Indeed, when pyridines were examined as substrates, their alkylation products were obtained, albeit in low yield. For example, pyridine itself led to the various possible isomers: in positions 2- (5%), 3- (3%), and 4- (1%). On the other hand, perfluoroalkylation of 1-methylpyrrole was regioselective as in the case of the thermal alkylation by perfluoroalkyl iodides.[8] For example, the 2-trifluoromethylation product was obtained in 52% yield [equation (1)].



(1)

Perfluoroalkylation in the Presence of Sodium Dithionite.—For the perfluoroalkylation of aromatic compounds, we used approximately a stoicheiometric quantity of sodium dithionite in the presence of disodium hydrogen phosphate in aqueous DMF. Reactions with trifluoromethyl bromide were performed under a slight pressure at 65 °C, and those of liquid perfluoroalkyl iodides were performed at atmospheric pressure and at 20 °C. However, in some experiments we observed that a decimolar quantity of sodium dithionite was sufficient to induce

Table 1.

Aromatic Compound	Method	Perfluoroalkyl halide	Products *ortho* (% yield)	Products *para* (% yield)	Products total (% yield)[a]
Aniline	A[b]	CF_3Br	36	20	56
Aniline	B[c]	CF_3Br	32	17	49[d]
Aniline	B[e]	C_2F_5I	21	16	37[f]
Aniline	A[g]	C_4F_9I	30	30	60
Aniline	B[g]	$C_8F_{17}I$	27	27	54
4-Methylaniline	A[b]	CF_3Br	30		30
2-Methylaniline	A[b]	CF_3Br	15	15	30
3-Methylaniline	A[b]	CF_3Br	18[h] + 12[i]	18	58
2-Chloroaniline	A[b]	CF_3Br	21	21	42[j]
3-Chloroaniline	A[b]	CF_3Br	12[h] + 15[i]	14	41
3-Methoxyaniline	A[b]	CF_3Br	21[h] + 24[i]	24	69[k]
1,3-Diaminobenzene	A[b]	CF_3Br	16	7	23[l]
N,N-Diethylaniline	A[b]	CF_3Br	18	18	36
1-Aminonaphthalene	A[b]	CF_3Br	30	20	50
3-Aminophenol	A[b]	CF_3Br	17[h] + 17[i]	17	51[m]
2-Aminophenol	A[b]	CF_3Br	19	30	49
Phenol	A[b]	CF_3Br	20	10	30
Phenol	B[c]	CF_3Br	20	8	28
3-Chlorophenol	A[b]	CF_3Br	17[h] + 19[i]	12	48
3-Methylphenol	A[b]	CF_3Br	26[h] + 16[i]	24	66
3-Methoxyphenol	A[b]	CF_3Br	25[h] + 25[i]	25	75

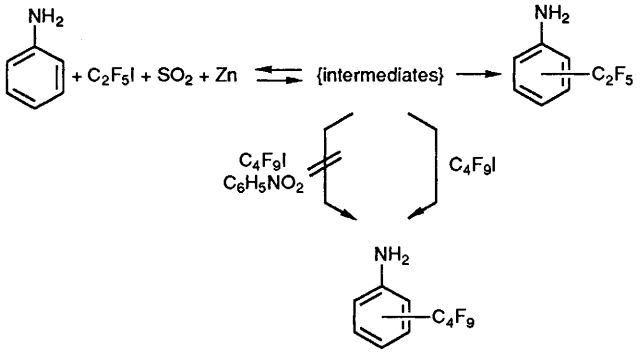
Method A: Zn–SO_2; Method B: sodium dithionite (general process). [a] Yields are given for isolated and purified isomers except for perfluorobutyl and perfluoro-octylaniline (GLC analysis). [b] Pressure 3–5 bar. [c] Pressure 2–4 bar; temperature 55 °C. [d] Bis(trifluoromethyl)anilines were also obtained: 2,6-isomer (2%); 2,4-isomer (4%). [e] Pressure 2–4 bar; temperature 65 °C. [f] Bis(trifluoroethyl)anilines were also obtained: 2,6-isomer (2%); 2,4-isomer (3%). [g] Atmospheric pressure. [h] *ortho*-Alkylation relative to both initial substituents. [i] Other *ortho*-alkylation product. [j] 2-Trifluoromethylaniline (14%) was also obtained. [k] 3-Methoxy-2,6-bis(trifluoromethyl)aniline (4%) was also obtained. [l] Bis-trifluoromethylation 13%. [m] Bis-trifluoromethylation 3%.

this perfluoroalkylation, provided that experiments with trifluoromethyl bromide were performed under higher pressure.

Trifluoromethylation of toluene was not selective and led to the various isomers of trifluoromethyltoluene: *ortho* (16%), *meta* (5%), and *para* (7%). The reaction of aniline led only to the *ortho* and *para* isomers of trifluoromethylaniline in 49% yield (Table 1). A few per cent of bis(trifluoromethyl)aniline was also obtained. The hydroxy group in the phenols oriented the alkylation also towards the *ortho* and *para* positions.

Perfluoro-octyl iodide gave equivalent amounts of *o*- and *p*-perfluoro-octylaniline (Table 1). The gaseous perfluoroethyl iodide was used under conditions similar to those of the reaction with trifluoromethyl bromide. Besides monopentafluoroethylated aniline, a few per cent of bis-perfluoroethylated products were obtained.

Trifluoromethylation of pyridine gave a poor yield of the various isomers of trifluoromethylpyridine: in positions 2- (4%), 3- (1%), and 4- (5%). Trifluoromethylation of pyrrole was regioselective in the 2-position (47% yield).

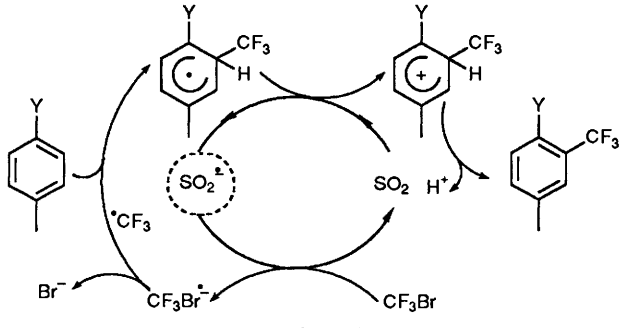


Scheme 3.

Discussion

These two methods of aromatic perfluoroalkylation showed similar trends and seemed to involve the same reactive intermediates. Strongly electron-donating substituents, such as amino groups, are necessary in order to get fair yields. In this case, the alkylation is oriented towards the electron-rich *ortho* and *para* positions. Similarly, trifluoromethylation of 1-methylpyrrole is regioselective at the 2-position. On the other hand, alkylation of toluene, or pyridine is not selective. These observations are compatible with the formation of an intermediate electrophilic perfluoroalkyl radical.

In order to confirm this hypothesis, several experiments were performed. In experiment A, half of the solution resulting from the reaction of sulphur dioxide and zinc, in a mixture of aniline, 2-methylpyridine and DMF, was transferred into a second flask containing nonafluorobutyl iodide. After being stirred for 30



Scheme 4.

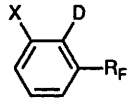
Table 2. NMR Data of trifluoroaromatic compounds.

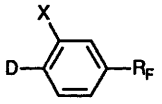
Compound	δ_F/ppm	δ_H(integration, multiplicity, *y*/Hz)
(2a)	−60.6(q)	7.6 (1 H, t, 7.5), 7.4 (1 H, d, 7.5), 7.24 (2 H, m), 2.47 (3 H, q, 1)
(2b)	−61.6(s)	7.35, (2 H, m), 7.45 (2 H, m), 2.41(s)
(2c)	−61.8(s)	7.5 (2 H, d), 7.25 (2 H, d, 8.1), 2.4(s)
(3a)	−63.8(s)	8.77 (1 H, d, 5.5), 7.45 (1 H), 7.36 (1 H, d), 2.67 (3 H, s)
(3b)	−62.2(s)	8.62 (1 H, d, 4.75), 7.84 (1 H, dd), 7.29 (1 H, d, 8), 2.89 (3 H, br s)
(3c)	−62(s)	8.77 (1 H, d), 8.2 (1 H, d, 8), 7.86 (1 H), 2.62 (3 H, s)
(3d)	−68(s)	7.73 (1 H, t), 7.46 (1 H, d, 7.7), 7.3 (1 H, d, 7.7), 2.64 (3 H, s)
(4a)	−63(s)	6.70 (2 H, m), 7.35 (2 H, m)
(4b)	−60(s)	7.46 (2 H, d, 8.5), 6.66 (2 H, d)
(5)	−63(s)	7.3 (1 H), 7.03 (1 H, d, 8.5), 6.7 (1 H), 2.3 (3 H, s)
(6a)	−62(s)	6.73 (1 H, t, 8.5), 7.33 (2 H, t), 2.17(s)
(6b)	−60(s)	7.33 (2 H, m), 6.73 (1 H, d, 8.5), 2.2 (3 H, s)
(8a)	−61(s)	7.3 (1 H, d, 8.5), 6.57 (2 H, d, 8.5), 2.25 (3 H, s)
(8b)	−53.5(q)	7.07, (1 H, t, 8.5), 6.05 (2 H, m), 2.33 (3 H, q, 3.3)
(8c)	−58(br s)	7.37 (1 H, d, 8.5), 6.43 (2 H, m) 2.33 (3 H br s)
(10a)	−62(s)	7.4 (2 H, d, 8), 6.7 (1 H, t)
(10b)	−60(s)	7.57, (1 H, br s) 7.3 (1 H, br d), 6.73 (1 H, d, 8.5)
(11a)	−62(s)	6.73 (2 H, m), 7.27 (1 H, br s)
(11b)	−54(s)	6.83 (3 H, m)
(11c)	−60(s)	7.41 (1 H, d, 8.5), 6.55 (2 H, m)
(13a)	−53.2(s)	7.17 (1 H, t), 6.37 (2 H, d, 8.5), 3.82 (3 H, s)
(13b)	−60.6(s)	7.3 (1 H, d, 8.5), 6.3 (m), 6.2 (1 H, br s), 3.78 (3 H, s)
(13c)	−60(s)	7.37 (1 H, d, 8.5), 6.3 (1 H, m), 6.22 (1 H, br s), 3.73 (3 H, s)
(15a)	−54(s)	6.93 (1 H, t), 6.0 (2 H, d, 8.25)
(15b)	−61.2(s)	7.3 (1 H, d, 8.5), 6.03 (1 H, m), 5.93 (1 H, br s)
(16a)	−62(s)	8–7.43 (5 H, m), 7.23 (1 H, d, 9)
(16b)	−59(s)	8.5–8.23 (1 H, m), 7.78–7.4 (4 H, m), 6.63 (1 H, d, 8.5)
(17a)	−58(s)	7.18 (2 H, m), 6.57 (2 H, m), 3.3 (4 H, q, 6.5), 1.08 (6 H, t)
(17b)	−60(s)	7.4 (2 H, d, 8.5), 6.57 (2 H, d), 3.27 (4 H, q, 6.5), 1.07 (3 H, t)
(19a)	−54.5(s)	7.08 (1 H, t), 6.33 (2 H, d, 8.25)
(19b)	−61(s)	7.27 (1 H, d, 9), 6.33 (1 H, br s), 6.23 (1 H, d)
(19c)	−60.6(s)	7.27 (1 H, d, 9), 6.27 (2 H, m)
(21a)	−62(s)	7.55 (1 H, t, 8.5), 6.02 (2 H, m)
(21b)	−59(s)	6.90 (2 H, m), 6.66 (1 H, d, 8.5)
(28a)	−61.6(s)	7.48 (2 H), 7 (2 H)
(28b)	−60.3(s)	7.53 (2 H, d), 6.93 (2 H, d, 8.5)
(29a)	−55(s)	7.23 (1 H, t, 8.5), 6.93 (2 H, m)
(29b)	−60.3(s)	7.4 (1 H, d, 8.5), 6.93 (2 H, m)
(29c)	−62(s)	7.53 (1 H, t, 8.5), 6.87 (2 H, m)
(30a)	−53.3(q)	7.27 (1 H, dd, 8 and 9) 6.8 (2 H, m), 2.43 (3 H, q, 3)
(30b)	−60(s)	7.4 (1 H, d, 8.5), 6.8 (2 H, m), 2.27 (3 H, s)
(30c)	−59(br s)	7.43 (1 H, d, 8.5), 6.7 (2 H, m), 2.37 (3 H, br s)
(31a)	−53.8(s)	7.33 (1 H, t, 8.5), 6.56 (2 H, m), 3.87 (3 H, s)
(31b)	−59(s)	7.43 (1 H, d, 8.5), 6.53 (2 H, m), 3.77 (3 H, s)
(31c)	−61(s)	7.43 (1 H, d, 8.5), 6.36 (2 H, m), 3.83 (3 H, s)
(35a)	−64.2(s)	8.77 (2 H, d, 5.3), 7.43 (2 H, d)
(35b)	−61.7(s)	8.87 (1 H, br s), 8.8 (1 H, br d, 6), 7.91 (1 H, br d, 8), 7.47 (1 H, dd)
(35c)	−62(s)	8.71 (1 H, br d, 5), 7.87 (1 H, td, 8 and 1.5), 7.67 (1 H, dt, 8 and 1.5), 7.49 (1 H, ddd, 8, 5, and 1.5)

min, the mixture was subjected to ^{19}F NMR analysis and showed the formation of the perfluorobutylaniline isomers. Consequently, an intermediate in the first solution was able to initiate the perfluoroalkylation. In experiment B, the same procedure was applied except that pentafluoroethyl iodide was bubbled, after sulphur dioxide, through the initial mixture prior to its transfer to the second flask. Besides pentafluoroethylanilines, nonafluorobutylanilines were detected. Formation of nonafluorobutylanilines was clearly inhibited by the electron scavenger nitrobenzene (Scheme 3).

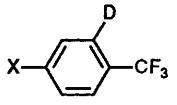
These observations can be interpreted as a radical aromatic alkylation (Scheme 4 written for the trifluoromethylation case). The cyclohexadienyl radical, issuing from the capture of the trifluoromethyl radical by the aromatic nucleus, is oxidized to its corresponding cation. The latter is aromatized to the end product by loss of a proton. The oxidant can be sulphur dioxide which is consequently reduced to its radical anion; this intermediate species is able to generate trifluoromethyl radicals (Scheme 2), thus maintaining a radical chain process. This idea that sulphur dioxide radical anion can be the intermediate in solution is also compatible with the sodium dithionite reaction because this salt is well known to dissociate easily (Scheme 2).

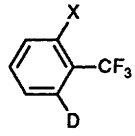
Conclusions.—The scope of this perfluoroalkylation induced by sulphur dioxide radical anion precursors is limited to electron-rich aromatic compounds. In contradistinction to other procedures, using perfluoroalkyl iodides for the alkylation of arylamines,[9,10] or nitrogen heterocyclic compounds,[8,11,12] this method includes the use of the cheap and easily available trifluoromethyl bromide. Even if the regioselectivity is only partial, this process constitutes the first direct trifluoromethylation of anilines and phenols by trifluoromethyl halides.[9] These

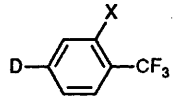




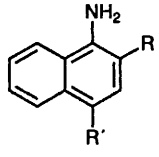
	R_F	D	X		R_F	D	X
(1)	CF_3	H	H	(2b)	CF_3	H	CH_3
(2a)	CF_3	CH_3	H	(2c)	CF_3	CH_3	H
(4a)	CF_3	NH_2	H	(4b)	CF_3	NH_2	H
(6a)	CF_3	NH_2	CH_3	(6b)	CF_3	NH_2	CH_3
(10a)	CF_3	NH_2	Cl	(10b)	CF_3	NH_2	Cl
(17a)	CF_3	$N(C_2H_5)_2$	H	(17b)	CF_3	$N(C_2H_5)_2$	H
(21a)	CF_3	NH_2	OH	(21b)	CF_3	NH_2	OH
(22a)	CF_2CF_3	NH_2	H	(22b)	CF_2CF_3	NH_2	H
(23a)	C_4F_9	NH_2	H	(23b)	C_4F_9	NH_2	H
(28a)	CF_3	OH	H	(28b)	CF_3	OH	H
(34a)	C_8F_{17}	NH_2	H	(34b)	C_8F_{17}	NH_2	H



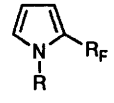




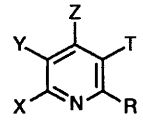
	D	X		D	X		D	X
(8a)	NH_2	CH_3	(8b)	NH_2	CH_3	(8c)	NH_2	CH_3
(11a)	NH_2	Cl	(11b)	NH_2	Cl	(11c)	NH_2	Cl
(13b)	NH_2	OCH_3	(13a)	NH_2	OCH_3	(13c)	NH_2	OCH_3
			(15a)	NH_2	NH_2	(15b)	NH_2	NH_2
(19b)	NH_2	OH	(19a)	NH_2	OH	(19c)	NH_2	OH
(29b)	OH	Cl	(29a)	OH	Cl	(29c)	OH	Cl
(30b)	OH	CH_3	(30a)	OH	CH_3	(30c)	OH	CH_3
(31b)	OH	OCH_3	(31a)	OH	OCH_3	(31c)	OH	OCH_3



	R	R′
(16a)	CF_3	H
(16b)	H	CF_3

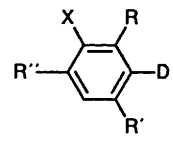


	R	R_F
(24)	H	CF_3
(25)	CH_3	CF_3
(26)	CH_3	C_2F_5
(27)	CH_3	C_8F_{17}



	R	T	X	Y	Z
(3a)	CH_3	H	H	H	CF_3
(3b)	CH_3	CF_3	H	H	H
(3c)	CH_3	H	H	CF_3	H
(3d)	CH_3	H	CF_3	H	H
(35a)	H	H	H	H	CF_3
(35b)	H	H	H	CF_3	H
(35c)	H	H	CF_3	H	H

trifluoromethyl derivatives are important intermediates for the synthesis of drugs and agrochemicals.[13,*]



	D	R	R′	R″	X
(5)	NH_2	CF_3	H	CH_3	H
(12)	NH_2	CF_3	CF_3	H	OCH_3
(14a)	NH_2	CF_3	H	CF_3	NH_2
(14b)	NH_2	H	CF_3	CF_3	NH_2
(18)	NH_2	CF_3	CF_3	H	OH
(32a)	NH_2	CF_3	H	CF_3	H
(32b)	NH_2	CF_3	CF_3	H	H
(33a)	NH_2	C_2F_5	C_2F_5	H	H
(33b)	NH_2	C_2F_5	H	C_2F_5	H

Experimental

^{1}H NMR spectra were recorded on a Bruker A 300 spectrometer with tetramethylsilane as internal standard. Fluorine NMR spectra were obtained on a Varian EM360L spectrometer (56.4 MHz) and were recorded in ppm (δ_F) downfield from $CFCl_3$ (solvent: $CDCl_3$). In most cases, fluorine signals were singlets, and this can give a good indication of the compounds' purity. Moreover, GLC analysis of purified products showed a purity >95%. It was not possible to use combustion analysis as the sole test of purity, owing to the formation of positional isomers. It appeared that the *ortho* isomers of trifluoromethylarylamines were extracted first when the medium was made progressively more acidic. Trifluoromethyl bromide was purchased from Setic Labo, trifluoromethyl iodide from Fluorochem Ltd., DMF, pyridine, and organic reactants (distilled before use) from Aldrich, and zinc from Prolabo. Perfluoroalkyl iodides were generous gifts of Atochem. NMR spectra of mono-trifluoromethyl compounds are recorded in Table 2 and microanalysis in Table 3.

Method A: Reaction with Zinc–Sulphur Dioxide.—Trifluoromethylbenzene. A mixture of benzene (40 ml, 0.35 mol), DMF (100 ml), 2-methylpyridine (40 ml), zinc (5 g, 0.077 mol), and sodium 'metabisulphite' ($Na_2S_2O_5$) (20 g, 0.1 mol) was placed under reduced pressure in a thick glass reactor and thermostatted at 65 °C. Sulphur dioxide (20 g, 0.3 mol) was added. The mixture was stirred for 3 h under a pressure of trifluoromethyl bromide of between 7–8 bar. After filtration, the reaction mixture was poured into a mixture of ice (200 g) and conc. hydrochloric acid (60 ml). After extraction with diethyl ether, the extract was washed successively with 10% hydrochloric acid and brine, dried ($MgSO_4$), and evaporated; distillation of the residue at 102 °C gave a fraction containing benzene and trifluoromethylbenzene (**1**). Analysis by GLC on a 30% SE30 PAW column showed that the alkylated product was obtained in 17% yield; δ_F −64 (s).

Trifluoromethyltoluenes.[14] The experiment was repeated with toluene (40 ml, 0.38 mol). After distillation (b.p. 145 °C), the trifluoromethyltoluenes (15.3 g, 0.096 mol were separated by GLC on a preparative 30% SE30 PAW column at 100 °C: 2-trifluoromethyltoluene (**2a**) (5.5 g, 9%); 3-trifluoromethyltoluene (**2b**) (2.4 g, 4%); 4-trifluoromethyltoluene (**2c**) (5.5 g, 9%).

If the extraction was performed five times, 2-methyl-6-trifluoromethylpyridine (**3d**) (1.5 g) was also obtained in 2% yield; some DMF was also extracted.

* After completion of this manuscript, a report appeared describing a base-catalysed trifluoromethylation of quinones by trialkyl(trifluoromethyl)silanes and giving updated references: G. P. Stahly and D. R. Bell, *J. Org. Chem.*, 1989, **54**, 2873.

Table 2. Microanalyses.

Compound	Formula	Required (%)			Found (%)		
		C	H	N (or F)	C	H	N (or F)
(**3b**)	$C_7H_6F_3N$	52.18	3.75	8.69	52.1	3.6	8.5
(**4a**)	$C_7H_6F_3N$	52.18*	3.75*	8.69* (F 35.38)*	52.3	3.8	8.6 (F 35.2)
(**4b**)	$C_7H_6F_3N$	52.18*	3.75*	8.69*	52.1	3.6	8.5
(**5**)	$C_8H_8F_3N$	54.86	4.61	8.00	54.7	4.7	8.1
(**6b**)	$C_8H_8F_3N$	54.86	4.61	8.00	54.6	4.4	7.8
(**8c**)	$C_8H_8F_3N$	54.86	4.61	8.00	55.0	4.85	8.3
(**10a**)	$C_7H_5ClF_3N$	42.99	2.58	7.16	43.3	2.7	6.9
(**11c**)	$C_7H_5ClF_3N$	42.99	2.58	7.16	43.1	2.8	7.0
(**13a**)	$C_8H_8F_3NO$	50.26	4.22	7.33	50.3	4.2	7.0
(**14b**)	$C_8H_6F_6N_2$	39.35	2.48	11.48	39.6	2.7	11.7
(**15a**)	$C_7H_7F_3N_2$	47.73	4.01	15.91	48.0	3.8	16.2
(**16a**)	$C_{11}H_8F_3N$	62.56	3.82	6.33	62.7	3.9	6.5
(**17a**)	$C_{11}H_{14}F_3N$	60.82	6.50	6.45	61.0	6.6	6.4
(**18**)	$C_8H_5F_6NO$	39.20	2.06	5.71	39.5	2.3	6.0
(**19b**)	$C_7H_6F_3NO$	47.46	3.41	7.91	47.7	3.8	7.6
(**21a**)	$C_7H_6F_3NO$	47.46	3.41	7.91	47.5	3.6	8.0
(**22a**)	$C_8H_6F_5N$	45.51	2.86	6.63	45.55	3.0	6.7
(**25**)	$C_6H_6F_3N$	48.32*	4.06*	9.39*	48.5	4.2	9.1
(**28a**)	$C_7H_5F_3O$	51.86*	3.11*	(F 35.16)*	52.15	3.1	(F 35.4)
(**28b**)	$C_7H_5F_3O$	51.86	3.11	(F 35.16)	51.8	3.2	(F 35.0)
(**30c**)	$C_8H_7F_3O$	54.55	4.01		54.6	3.9	
(**31b**)	$C_8H_7F_3O_2$	50.01	3.67		49.9	3.8	
(**32a**)	$C_8H_5F_6N$	41.93	2.20	6.11	42.1	2.4	6.0
(**33b**)	$C_{10}H_5F_{10}N$	24.55	1.03	2.86	24.7	1.3	3.0
(**35c**)	$C_6H_4F_3N$	48.99	2.74	9.52	48.7	2.9	9.3

* *Calculated* values for *known* compounds.

2-*Methyl(trifluoromethyl)pyridines.* The same experiment was repeated in the absence of benzene. After five extractions with diethyl ether, the extracts were washed twice with brine, dried ($MgSO_4$), and evaporated; the following products were separated by GLC on a preparative DEGS WAW column at 130 °C: 2-methyl-4-trifluoromethylpyridine (**3a**) (0.8 g, 1%); 2-methyl-3-trifluoromethylpyridine (**3b**) (3.3 g, 4%); 2-methyl-5-trifluoromethylpyridine (**3c**) (2.0 g, 3%); 2-methyl-6-trifluoromethylpyridine[15] (**3d**) (1.7 g, 2%).

Trifluoromethylanilines. A mixture of an aniline, DMF (25 ml), 2-methylpyridine (10 ml), zinc (1 g, 0.015 mol), and $Na_2S_2O_5$ (10 g, 0.05 mol) were placed under reduced pressure in a thick glass flask and thermostatted at 20 °C. Sulphur dioxide (4 g, 0.06 mol) was added. The mixture was shaken for 2 h under a pressure of trifluoromethyl bromide of between 3–5 bar. The reaction was exothermic. After filtration, the reaction mixture was poured into a mixture of ice (50 g) and conc. hydrochloric acid (15 ml) and the product was steam distilled. The product was extracted with diethyl ether, and the extract was washed with brine, dried ($MgSO_4$), and purified to give the trifluoromethylanilines.

From aniline (10 g, 0.11 mol), distillation and control by GLC on a 30% SE30 PAW gave: 2-trifluoromethylaniline (**4a**) (6.3 g, 36%), b.p. 66 °C/14 mmHg (b.p. Aldrich 68 °C/15 mmHg) and 4-trifluoromethylaniline (**4b**) (3.4 g, 20%), b.p. 86 °C/14 mmHg (b.p. Aldrich 83 °C/15 mmHg).

From 4-methylaniline (10 g, 0.093 mol), distillation gave 4-methyl-2-trifluoromethylaniline (**5**) (4.9 g, 30%), b.p. 41 °C/0.5 mmHg.

From 2-methylaniline (10 g, 0.093 mol), distillation gave a mixture (4.5 g) which was separated by GLC on a 17% DEGS WAW preparative column at 170 °C: 2-methyl-6-trifluoromethylaniline[16] (**6a**) (2.5 g, 15%) and 2-methyl-4-trifluoromethylaniline[17] (**6b**) (2.4 g, 15%).

From 3-methylaniline (10 g, 0.093 mol), distillation gave a mixture (9.9 g) which was separated by GLC on a 17% DEGS WAW preparative column at 170 °C: 3-methylbis(trifluoromethyl)anilines (**7**) (three non-separated isomers) (1.0 g, 4%); δ_F −53.5, −54, −58.5, −61, and −63; 5-methyl-2-trifluoromethylaniline (**8a**) (2.0 g, 12%); 3-methyl-2-trifluoromethylaniline (**8b**) (2.9 g, 18%); 3-methyl-4-trifluoromethylaniline (**8c**) (2.8 g, 18%).

With 2-chloroaniline (10 g, 0.08 mol), the flask was shaken at 50 °C for 4 h. The resulting mixture was separated by column chromatography (silica/benzene): bis(trifluoromethyl)anilines (**9**) (1 g) (1:1 mixture of two non-separated isomers): δ_F −60.6, −61.2, −62.4, and −62.8; 2-chloro-6-trifluoromethylaniline (**10a**) (3.2 g, 21%); 2-chloro-4-trifluoromethylaniline[18] (**10b**) (3.2 g, 21%), identical with an authentic sample from Dr Desbois, Rhone-Poulenc; 2-trifluoromethylaniline (**4a**) (2.1 g, 14%); δ_F (in the mixture): −61.6 (s), identical with an authentic sample.

With 3-chloroaniline (10 g, 0.08 mol), the flask was shaken for 3 h. The resulting mixture was separated by GLC on a 30% SE30 PAW column at 220 °C: 5-chloro-2-trifluoromethylaniline[19] (**11a**) (2.3 g, 15%); 3-chloro-2-trifluoromethylaniline (**11b**) (1.8 g, 12%); 3-chloro-4-trifluoromethylaniline (**11c**) (2.1 g, 14%).

With 3-methoxyaniline (10 g, 0.08 mol), the resulting mixture was separated by silica column chromatography with benzene–ethyl acetate (9:1): 3-methoxy-2,6-bis(trifluoromethyl)aniline (**12**) (0.8 g, 4%); δ_F −53.3 and −60.8; δ_H 7.53 (1 H, d), 6.37 (1 H, d, *J* 8.5 Hz), and 3.87 (3 H, s); 3-methoxy-2-trifluoromethylaniline (**13a**) (3.3 g, 21%); 5-methoxy-2-trifluoromethylaniline[19] (**13b**) (3.7 g, 24%); 3-methoxy-4-trifluoromethylaniline (**13c**) (3.7 g, 24%).

With 1,3-diaminobenzene (10 g, 0.092 mol), the resulting mixture was separated by silica column chromatography with benzene–ethyl acetate (9:1); the yield [in brackets] was obtained with 2,6-dimethylpyridine (10 ml) instead of methyl-

pyridine: 1,3-diamino-2,4-bis(trifluoromethyl)benzene (**14a**) (1.6 g, 7%), m.p. 40 °C [17%]; δ_F −54.0 (s); −60.5 (s); δ_H 7.27 (1 H, d, *J* 8.25 Hz) and 5.98 (1 H, d); *m/z* 244, 224, 204, 197, and 177; 1,5-diamino-2,4-bis(trifluoromethyl)benzene (**14b**) (1.4 g, 6%), m.p. 85 °C [7%]; δ_F −60.7 (s); δ_H 7.5 (1 H, s) and 5.95 (1 H, s); *m/z* 244, 224, 204, 197, and 177; 1,3-diamino-2-trifluoromethylbenzene (**15a**) (2.6 g, 16%), m.p. 66 °C [3%]; *m/z* 176 and 156; 1,3-diamino-4-trifluoromethylbenzene[20] (**15b**) (1.1 g, 7%) [8%]; *m/z* 176 and 156.

With 1-aminonaphthalene (10 g, 0.07 mol), the resulting mixture was separated by silica column chromatography with benzene: 1-amino-2-trifluoromethylnaphthalene (**16a**) (4.3 g, 30%); 1-amino-4-trifluoromethylnaphthalene[21] (**16b**) (3.0 g, 20%).

With *N,N*-diethylaniline (10 g, 0.067 mol), the reaction time was 3 h. Distillation gave an equimolar mixture (5.3 g) which was separated by GLC on a 30% SE30 PAW preparative column at 170 °C *N,N*-diethyl-2-trifluoromethylaniline (**17a**) (2.6 g, 18%); *m/z* 217, 202, 183, 174, 154, and 122; *N,N*-diethyl-4-trifluoromethylaniline (**17b**) (2.5 g, 18%); *m/z* 217 and 202.

With 3-aminophenol (10 g, 0.092 mol), the resulting mixture was separated by silica column chromatography with benzene–ethyl acetate (9:1): 3-amino-2,4-bis(trifluoromethyl)phenol (**18**) (0.5 g, 3%); δ_F −54 and −61; δ_H 7.47 (1 H, d) and 6.33 (1 H, d); 3-amino-2-trifluoromethylphenol (**19a**) (2.8 g, 17%), m.p. 121 °C; 3-amino-4-trifluoromethylphenol (**19b**) (2.8 g, 17%), m.p. 101 °C; 5-amino-2-trifluoromethylphenol (**19c**) (2.8 g, 17%), m.p. 131 °C.

With 2-aminophenol (10 g, 0.092 mol), the resulting mixture was separated by silica column chromatography with benzene–ethyl acetate (9:1): 2-aminobis(trifluoromethyl)phenols (**20**) (2 g, 9%), δ_F −57.7, −60.6, −61.6, and −63.6; 2-amino-3-trifluoromethylphenol (**21a**) (5.4 g, 19%); 2-amino-5-trifluoromethylphenol (**21b**) (3 g, 30%).

Pentafluoroethylanilines. Trifluoromethyl bromide was replaced by pentafluoroethyl iodide (30 g). From aniline (10 g, 0.11 mol), pentafluoroethylanilines (3.1 g) were obtained which were separated by GLC on a 17% DEGS WAW preparative column at 170 °C: 2-pentafluoroethylaniline (**22a**) (1.7 g, 7%), δ_F −84 (3 F), and −113 (2 F); δ_H 7.23 (2 H) and 6.77 (2 H); 4-pentafluoroethylaniline[22] (**22b**), (1.6 g, 7%), δ_F −84 (3 F) and −113.6 (2 F); δ_H 7.43 (2 H) and 6.73 (2 H).

Nonafluorobutylanilines. A mixture of aniline (10 g, 0.11 mol), DMF (25 ml), 2-methylpyridine (10 ml), zinc (1 g, 0.015 mol), and $Na_2S_2O_5$ (10 g, 0.05 mol) was placed under a 50:50 gaseous argon–sulphur dioxide mixture. Nonafluorobutyl iodide (35 g, 0.1 mol) was added to the stirred mixture at 10 °C. After filtration, the reaction mixture was poured into ice (50 g)–conc. hydrochloric acid (15 ml). The mixture was extracted with diethyl ether, and the extract was washed with brine, and then dried ($MgSO_4$) to afford, after work-up, an equimolar mixture (20 g), which was separated by silica column chromatography with benzene (20.3 g, 60%): 2-nonafluorobutylaniline (**23a**), δ_F −82 (3 F), −111 (2 F), −123 (2 F), and −127 (2 F); δ_H 7.36 (2 H) and 6.87 (2 H); 4-nonafluorobutylaniline (**23b**), δ_F −82 (3 F), −111 (2 F), −123 (2 F), and −127 (2 F); δ_H 7.5 (2 H) and 6.77 (2 H).

2-Trifluoromethylpyrrole.[11] With pyrrole (10 g, 0.15 mol), the reaction time was 3 h. After continuous extraction with pentane during 24 h, a mixture of pyrrole, DMF, and 2-trifluoromethylpyrrole (**24**) (6 g, 0.044 mol) was separated from the reaction product by GLC on a 17% DEGS WAW preparative column at 140 °C (3.1 g, 15%), δ_F −58 (s); δ_H 6.9 (1 H), 6.67 (1 H), and 6.28 (1 H).

N-Methyl-2-trifluoromethylpyrrole.[11] With *N*-methylpyrrole (10 g, 0.12 mol), the reaction time was 3 h; after extraction with diethyl ether *N*-methyl-2-trifluoromethylpyrrole (**25**) (9.3 g, 52%) was distilled from the reaction product at 116 °C, δ_F −58 (s); δ_H 6.76 (1 H), 6.66 (1 H), 6.17 (1 H), and 3.77 (3 H, s).

N-Methyl-2-pentafluoroethylpyrrole.[8] Trifluoromethyl bromide was replaced by pentafluoroethyl iodide (30 g) in the *N*-methylpyrrole (10 g, 0.12 mol) condensation. The reaction time was 3 h; after extraction with diethyl ether, *N*-methyl-2-pentafluoroethylpyrrole (**26**) (7.3 g, 30%) was distilled from the reaction product at 126–127 °C; δ_F −84 (3 F) and −106 (2 F, *J* 3.5 Hz); δ_H 6.76 (1 H), 6.63 (1 H), 6.23 (1 H), and 3.76 (3 H, s).

N-Methyl-2-perfluoro-octylpyrrole.[8] A mixture of *N*-methylpyrrole (10 g, 0.12 mol), DMF (25 ml), 2-methylpyridine (10 ml), zinc (1 g, 0.015 mol), and $Na_2S_2O_5$ (10 g, 0.05 mol) was placed under a 50:50 gaseous argon–sulphur dioxide mixture. Perfluoro-octyl iodide (68 g, 0.12 mol) was added to the stirred mixture at 10 °C. After filtration, the reaction mixture was poured into ice (50 g)–conc. hydrochloric acid (15 ml). The product was extracted with diethyl ether, and the extract was washed with brine, then dried ($MgSO_4$) to afford, after work-up, *N*-methyl-2-perfluoro-octylpyrrole (**27**) (30.8 g, 50%) which was distilled at 72–73 °C/15 mmHg; δ_F −82 (3 F), −105 (2 F), and −123–128 (12 F); δ_H 6.83 (1 H), 6.5 (1 H), 6.23 (1 H), and 3.78 (3 H, s).

Trifluoromethylphenols. Following the general method with anilines, phenol (10 g, 0.106 mol) was treated for 4 h at 60 °C. After extraction, distillation gave 2-trifluoromethylphenol (**28a**) (3.5 g, 20%), b.p. 147–148 °C (b.p. Aldrich 147–148 °C). The residue was purified by GLC: in addition to unchanged phenol, it contained 4-trifluoromethylphenol (**28b**) (1.7 g, 10%).

3-Chlorophenol (10 g, 0.078 mol) was treated for 4 h at 60 °C. The resulting mixture was separated by GLC on a 30% SE30 PAW column, at 210 °C: 3-chloro-2-trifluoromethylphenol (**29a**) (2.6 g, 17%); 5-chloro-2-trifluoromethylphenol (**29b**) (2.9 g, 19%); 3-chloro-4-trifluoromethylphenol (**29c**) (1.8 g, 12%).

3-Methylphenol (10 g, 0.093 mol) was treated for 4 h at 60 °C. The resulting mixture was separated by distillation: 3-methyl-2-trifluoromethylphenol (**30a**) (4.2 g, 26%); b.p. 77–79 °C at 23 mmHg; 5-methyl-2-trifluoromethylphenol (**30b**) (2.6 g, 16%); b.p. 84–86 °C at 23 mmHg. The residue was purified by GLC: in addition to the unchanged phenol, it contained 3-methyl-4-trifluoromethylphenol (**30c**) (3.9 g, 24%).

3-Methoxyphenol (10 g, 0.081 mol) was treated for 3 h at 60 °C. The resulting mixture was separated by GLC on a 30% SE30 PAW column, at 210 °C: 3-methoxy-2-trifluoromethylphenol (**31a**) (3.9 g, 25%); 5-methoxy-2-trifluoromethylphenol (**31b**) (3.9 g, 25%); 3-methoxy-4-trifluoromethylphenol (**31c**) (3.9 g, 25%).

Reaction With Sodium Dithionite.—Trifluoromethylanilines and phenols. A mixture of aniline (10 g, 0.11 mol), DMF (50 ml), water (15 ml), sodium dithionite (10 g, 0.057 mol), and disodium hydrogen phosphate (8 g, 0.056 mol) was placed under reduced pressure in a thick glass flask and thermostatted at 65 °C. The mixture was shaken for 2 h under a pressure of trifluoromethyl bromide of 3–5 bar. The reaction mixture was poured into water (100 g) and was steam distilled. The product was extracted with diethyl ether, and the extract was washed with brine, and then dried ($MgSO_4$); distillation (and control by GLC on a 30% SE30 PAW column) gave 2-trifluoromethylaniline (**4a**) (4.0 g, 32%), b.p. 66 °C/14 mmHg (b.p. Aldrich 68 °C/15 mmHg); 4-trifluoromethylaniline (**4b**) (1.9 g, 11%), b.p. 86 °C/14 mmHg (b.p. Aldrich 83 °C/15 mmHg); 2,4-bis(trifluoromethyl)aniline (**32a**) (1 g, 4%), δ_F −60.8 (s) and −64 (s); δ_H 7.73 (1 H, br s), 7.53 (1 H, d, *J* 8.5 Hz), and 6.67 (1 H, d); 2,6-bis(trifluoromethyl)aniline[23] (**32b**) (0.5 g, 2%), δ_F −63.6 (s); δ_H 7.67 (2 H, d, *J* 8.5 Hz) and 6.83 (1 H, t).

The experiment was repeated with phenol (9.4 g, 0.10 mol) instead of aniline, at 65 °C. After steam distillation, distillation gave: 2-trifluoromethylphenol (**28a**) (3.4 g, 20%), b.p. 147–

148 °C (b.p. Aldrich 147–148 °C); 4-trifluoromethylphenol (**28b**) (1.4 g, 8%), b.p. 183 °C.

Pentafluoroethylanilines.[22] The experiment was repeated, but trifluoromethyl bromide was replaced by pentafluoroethyl iodide (1 bar). After steam distillation, separation by GLC on a 17% DEGS WAW preparative column at 170 °C gave: 2-pentafluoroethylaniline (**22a**) (4.4 g, 21%); 4-pentafluoroethylaniline (**22b**) (3.5 g, 16%); 2,6-bis(pentafluoroethyl)aniline (**33a**) (0.5 g, 2%), δ_F −84 (6 F) and −114 (4 F); δ_H 7.83 (2 H, d, *J* 8.5 Hz) and 6.67 (1 H, t); 2,4-bis(pentafluoroethyl)aniline (**33b**) (1.1 g, 3%), δ_F −84 (6 F), −113.6 (2 F), and −114 (2 F); δ_H 7.83 (1 H, br s), 7.5 (1 H, d, *J* 8.5 Hz), and 6.70 (1 H, d).

Heptadecafluoro-octylanilines. A mixture of aniline (1 g, 0.011 mol), DMF (5 ml), water (1.5 ml), sodium dithionite (1 g, 0.015 mol), disodium hydrogen phosphate (1 g), and perfluoro-octyl iodide (5.5 g, 0.01 mol) was stirred at 10 °C for 10 h. The reaction mixture was poured into ice (10 g)–conc. hydrochloric acid (5 ml). The mixture was extracted with diethyl ether, and the extract was washed with brine, then dried ($MgSO_4$), to afford, on work-up, an equimolar mixture (2.8 g) which was analysed by GLC with a 30% SE30 column: 2-heptadecafluoro-octylaniline (**34a**) (1.4 g, 27%), δ_F −82 (3 F), −110 (2 F), −124 (10 F), and −127 (2 F); 4-hepta decafluoro-octylaniline (**34b**) (1.4 g, 27%), δ_F −82 (3 F), −110.2 (2 F), −124 (10 F), and −127 (2 F).

Trifluoromethylbenzene. The experiment was repeated with benzene (10 ml, 0.14 mol), DMF (50 ml), 20% aq. ammonia (15 ml), and sodium dithionite (10 g, 0.057 mol) at 65 °C. After distillation at 102 °C, GLC analysis showed that trifluoromethylbenzene (**1**) had been obtained in 22% yield.

Trifluoromethyltoluenes.[14] The experiment was repeated with toluene (10 ml, 0.12 mol), DMF (50 ml), water (15 ml), dipotassium hydrogen phosphate (10 g), and sodium dithionite (10 g, 0.057 mol) at 65 °C. After distillation at 145 °C, analysis and purification by GLC gave: 2-trifluoromethyltoluene (**2a**) (2.8 g, 16%); 3-trifluoromethyltoluene (**2b**) (0.9 g, 5%); 4-trifluoromethyltoluene (**2c**) (1.2 g, 7%).

Trifluoromethylpyridines.[14] The experiment was repeated with pyridine (50 ml, 0.65 mol), water (15 ml), dipotassium hydrogen phosphate (10 g), and sodium dithionite (10 g, 0.057 mol) at 65 °C. After five extractions with diethyl ether, the combined extracts were washed twice with brine, dried ($MgSO_4$), and worked up; distillation and a final purification by GLC on a preparative DEGS WAW column, gave the following products: 4-trifluoromethylpyridine (**35a**) (4.8 g, 5%), b.p. 108–110 °C; 3-trifluoromethylpyridine (**35b**) (0.8 g, 1%), b.p. 110–113 °C; 2-trifluoromethylpyridine (**35c**) (3.8 g, 4%), b.p. 140 °C.

Trifluoromethylanilines: catalytic process. A mixture of aniline (28 g, 0.3 mol), DMF (150 ml), water (100 ml), sodium dithionite (5.3 g, 0.03 mol), and disodium hydrogen phosphate (43 g, 0.3 mol) were placed under reduced pressure in a stainless steel flask and thermostatted at 55 °C. The mixture was shaken for 1.5 h under trifluoromethyl bromide (13 bar). The reaction mixture was poured into water (100 g) and was steam distilled. After extraction with diethyl ether, the extract was washed with brine, then dried ($MgSO_4$) and worked up; distillation gave: 2-trifluoromethylaniline (**4a**) (9.2 g, 19%), b.p. 66 °C/14 mmHg; 4-trifluoromethylaniline (**4b**) (4.2 g, 10%), b.p. 86 °C/14 mmHg; 2,4-bis(trifluoromethyl)aniline (**32a**) (0.7 g, 1%); 2,6-bis(trifluoromethyl)aniline (**32b**) (0.3 g, 0.5%).

2-Trifluoromethylpyrrole: catalytic process. The previous experiment was repeated with pyrrole (20 g, 0.3 mol) instead of aniline. After extraction with diethyl ether, the extract was washed with brine, dried ($MgSO_4$), and worked up; distillation gave 2-trifluoromethylpyrrole (**24**) (19.0 g, 47%).

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