

CHEMISTRY OF ORGANIC FLUORINE COMPOUNDS. XII.*

RADICAL ADDITION OF TRIMETHYLAMINE
AND TRIETHYLAMINE TO TRIFLUOROCHLOROETHYLENE

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The reaction of trimethyl- and triethylamine with trifluorochloroethylene induced by γ -irradiation (^{60}Co) or UV light was found to yield, by trifluorochloroethylation of the α - and α,α' -positions of the alkyl groups, 4-methyl-1,2,2-trifluoro-1-chloro-4-azapentane (*III*) and 4-methyl-1,2,2,6,6,7-hexafluoro-1,7-dichloro-4-azaheptane (*IX*), and 3-methyl-4-ethyl-1,2,2-trifluoro-1-chloro-4-aza-hexane (*IV*) and 3,5-dimethyl-4-ethyl-1,2,2,6,6,7-hexafluoro-1,7-dichloro-4-azaheptane (*X*), respectively. In both cases 1 : 2 telomers were also detected. Secondary reaction products were the amines formed by radical splitting-off of chlorine atoms under the action of trimethyl- or triethylamine.

In a previous communication¹ we described the products of a radical addition of dimethylisopropylamine to trifluorochloroethylene. As an extension of this study, in the present work we have studied the addition of trimethylamine (*I*) and triethylamine (*II*) to trifluorochloroethylene initiated by γ -irradiation (^{60}Co) and by UV light. As the main products of both addition reactions we have isolated tertiary amines which contained one (1 : 1 adducts) and two (1 : 2 adducts) trifluorochloroethylene units attached to the α - or α,α' -positions of the alkyl groups. The addition of trimethylamine (*I*) was initiated only by γ -irradiation (^{60}Co) (ref.²) and yielded 4-methyl-1,2,2-trifluoro-1-chloro-4-azapentane (*III*, 1 : 1 adduct) and 4-methyl-1,2,2,6,6,7-hexafluoro-1,7-dichloro-4-azaheptane (*IX*, 1 : 2 adduct). Both γ -induced and UV light-induced addition² of triethylamine gave the same products, 3-methyl-4-ethyl-1,2,2-trifluoro-1-chloro-4-azaheptane (*IV*, 1 : 1 adduct) and 3,5-dimethyl-4-ethyl-1,2,2,6,6,7-hexafluoro-1,7-dichloro-4-azaheptane (*X*, 1 : 2 adduct). The individual amines were obtained by rectification. Gas chromatographic analysis of the intermediate fractions revealed that in both reactions small amount of other substances are also formed. In the fraction boiling 35–80°C/16 Torr, which was obtained by rectification of the products of the addition of trimethylamine, we have found – besides amines *III* and *IX* – two further compounds which were isolated by gas chromato-

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graphy and were identified as 6-methyl-1,2,2,3,4,4-hexafluoro-1-chloro-6-azaheptane (*XIII*) and dimethylamide of fluorochloroacetic acid (*VII*). In the lower boiling fractions collected during rectification of products of the addition of triethylamine we have found that adduct *IV* is accompanied by 3-methyl-4-ethyl-1,2,2-trifluoro-4-azahexane (*XIV*). The higher-boiling fraction of b.p. 69–120°C/15 Torr contained, along with amines *IV* and *X*, also 5-methyl-6-ethyl-1,2,2,3,4,4-hexafluoro-1,3-dichloro-6-aza-octane (*XII*, 1 : 2 telomer) and the reduction product of amine *X*, 3,5-dimethyl-4-ethyl-1,2,2,6,6,7-hexafluoro-1-chloro-4-azaheptane (*XVI*), in the ratio c. 1 : 2. Amines *XII* and *XVI* were identified without isolation by mass spectrometry. We have similarly detected trace amounts of some other reduction products, 5-methyl-6-ethyl-1,2,2,3,4,4-hexafluoro-1-chloro-6-aza-octane (*XV*) and 3,5-dimethyl-4-ethyl-1,2,2,6,6,7 hexafluoro-4-azaheptane (*XVII*).

In explaining the formation of the individual products we assume that interaction of UV light or γ -irradiation with a solution of trifluorochloroethylene in tertiary amine *I* or *II* brings about homolytic cleavage of the α -C—H bond^{3,4}, yielding radicals *Ia*, *Ila*, respectively, which add to the difluoromethylene group of trifluorochloroethylene to give 1 : 1 adduct-radicals *IIIa* and *IVa*, respectively. The formation of other tertiary amines can be accounted for by transformations of the above adduct-radicals. Chain transfer to the solvent (amine *I* or *II*) leads to 1 : 1 adducts *III* and *IV* and solvent-radicals *Ia* and *Ila*. The addition to other molecule of trifluorochloroethylene gives 1 : 2 telomer-radicals *XIa* and *XIIa* respectively, which by chain transfer to the starting amine give 1 : 2 telomers *XI* and *XII*. Owing to the suitable conformation the radicals *IIIa* and *IVa* can achieve, they can be transformed also to 1 : 1 adduct-radicals *IXa* and *Xa*, respectively, by 1,5-hydrogen shift from their α' -position¹. These, by the addition to other molecule of trifluorochloroethylene form 1 : 2 adduct-radicals *IXb* and *Xb*, respectively. Radicals *IXb* and *Xb* give 1 : 2 adducts *IX* and *X* and new solvent-radicals *Ia* and *Ila* by chain transfer to the starting amine. In the addition of trimethylamine (*I*) we have isolated from the reaction mixture also the amide *VII*. This indicates that, in addition to homolytic cleavage of α -C—H bonds, also homolytic splitting of the C—N bond is taking place⁵, even though to a lesser extent. The latter reaction gives the radical *Ib* which then by the addition and transfer reactions (*Ib* \rightarrow *IIIb* \rightarrow *V*) yields the amine *V*. This amine, because of the high reactivity of its fluorine atoms in the α -position to nitrogen⁶, undergoes further transformation, e.g. on contact with air moisture, affording the amide *VII*. An analogous splitting of the C—N bond of triethylamine under the formation of the radical *Ila* cannot be ruled out³, even though we were unable to detect the presence of either the amine *VI* or the amide *VIII*.

By contrast with the addition of dimethylisopropylamine¹, in the reaction of amines *I* and *II* we have observed the formation of small amounts of 1 : 2 telomer products *XI* and *XII*, respectively. Although not directly proved, the presence of the amine *XI* can be inferred from the isolated reduction product *XIII*. We believe

that the formation of the 1 : 2 telomers is rendered possible by a decreased reactivity of the hydrogen atoms of the methyl groups of amine *I* or the α -hydrogen atoms of amine *II*. The 1 : 1 adduct-radicals *IIIa* or *IVa* formed may undergo further reactions, chain termination by transfer to solvent, 1,5-chain shift to the α' -position of the alkyl group, and also the addition of radicals *IIIa* and *IVa* to other molecules of trifluorochloroethylene, *i.e.* telomerization.

It is interesting to compare molar amounts of 1 : 1 and 1 : 2 addition products for individual amines: dimethylisopropylamine¹, the ratio, 1.24 (UV-initiation) and 1.35 (γ -irradiation); triethylamine 2.04 (UV-initiation) and 2.21 (γ -irradiation); trimethylamine 26.0. This ratio is the measure of the ease with which the intramolecular 1,5-hydrogen shift takes place in the formed 1 : 1 adduct-radicals, and it increases with decreasing reactivity of the C—H bonds in the α -position of the alkyl groups (isopropyl > ethyl > methyl).

The amines *XIII*–*XVII* are formed as secondary products of the reaction by radical reduction of C—Cl bonds in the initially formed amines *XI*, *IV*, *XII*, and *X* in a solution of trimethylamine (the amine *XIII*) or triethylamine (the amines *XIV*–*XVII*). The reduction of C—Hal bonds in halogeno-substituted methanes under the action of UV light on their solutions in primary and tertiary amines has already been reported^{7,8}. We have observed^{9,10} the radical reduction of C—Cl bonds of —CFCl— groups in the telomers obtained in the addition of alcohols to trifluorochloroethylene in 2-propanol; the reaction did not proceed, however, with the —CFClH groups. Of the reduction products in the addition of trimethylamine we have isolated only the amine *XIII*, which was identified on the basis of its PMR and mass spectra. The presence of amines *XIV*, *XVI*, and *XVII* indicates that in triethylamine (*II*) also C—Cl bonds in the —CHClF groups suffer reduction. This reduction, independently of the addition, was proved by irradiating 1 : 1 adduct *IV* by UV light in triethylamine solution; as shown by chromatography and mass spectrometry, the so prepared amine *XIV* was identical with the amine *XIV*, which accompanied the amine *IV* in the reaction mixture after the addition. The 1 : 2 adduct *X* was also irradiated in triethylamine solution, and by mass spectrometry combined with gas chromatography, besides the unreacted starting amine *X*, the main products were identified as amines *XVI* and *XVII*, which were identical in retention times and mass spectra with the amines *XVI* and *XVII* found in the reaction mixture after the addition.

The structure of compounds *III*, *IX*, *XIII*, *VII*, *IV*, *X*, and *XIV* was determined on the basis of elemental analysis (Table I), PMR (Table II) and mass spectra. The structure of most of the reduction products, above all amines *XIV*, *XV*, *XVI*, *XII*, and *XVII*, was inferred only from their mass spectra. The PMR spectra of amines *III* and *IX* show the signal of proton of the terminal —CFClH group as characteristic couple of doublets of doublets. The mass spectrum of amine *III* agrees well with the suggested structure. The spectrum exhibits only two intense ions m/e 42 and 58, the intensity of others being below 8%. The molecular ion m/e 175 is accompanied by the ion $(M-1)^+$ of practically the same intensity. From the ratio of intensities of m/e 175 and 177, or 174 and 176 it is obvious¹¹ that substance *III* contains one chloride atom and odd number

of nitrogen atoms. The fragmentation of the molecular ion (proved by metastable ions) gives rise to the ions $(M-35)^+$ (m/e 140) and $(M-68)^+$ (m/e 107), neither of them containing chlorine. The origin of the ions m/e 58 and m/e 42 is not clear from the spectrum, it can be assumed, however, that the ions correspond to trimethyl radical and its fragment¹², respectively. In the mass spectrum of 1 : 2 adduct *IX* we have observed the molecular ion m/e 291. From the ratio of intensities of the group of ions around m/e 291 one can conclude that the molecule contains two chlorine atoms¹¹ and odd number of nitrogen atoms. Fragmentation of the molecular ion (proved by metastable ions) leads to the formation of ions $(M-35)^+$ and $(M-19)^+$, respectively, which have one or two chlorine atoms, respectively. The most intense fragment is that of m/e 174 ($(M-117)^+$), with one chlorine atom. Further intense ions are those of m/e 42, 43, 57 and 67, together with 106 and 107, similarly as in the spectrum of compound *III*. The ion m/e 58 is missing; instead, the ion m/e 57 is now appearing. The above data and the ratios of the areas of signals of individual protons in the PMR spectrum (2 : 4 : 3) confirm the suggested structure for amine *IX* and rule out the second possible structure of 1 : 2 telomer *XI*. In the mass spectrum of amine *XIII* the molecular ion m/e 257 forms with neighbouring ions the group which is characteristic of one chlorine atom in the molecule¹¹. The most intense ion is m/e 58, analogously as in *III*; the intensities of other ions do not exceed 20 rel.% (with respect to the intensity of the former ion); of them, more significant ones are m/e 42, 43, 44, 51, 67, 107, $(M-67)^+$, $(M-35)^+$, and $(M-19)^+$. The foregoing confirms the structure of amine *XIII*. Based on characteristic signals for HCFCl- and CHF- groups in the PMR spectrum¹⁰ (Table II) and on the observed higher reactivity of the chlorine

TABLE I

Analyses of the Products of Radical-Induced Addition of Trimethylamine (*I*) and of Triethylamine (*II*) to Trifluorochloroethylene

Compound	Formula (m.w.)	Calculated/Found				
		% C	% H	% Cl	% F	% N
<i>III</i>	C ₅ H ₉ ClF ₃ N (175.6)	34.20	5.17	20.19	32.46	7.98
		34.43	5.25	19.74	32.88	7.95
<i>VII</i>	C ₄ H ₇ ClFNO (139.6)	34.42	5.05	25.41	13.61	10.04
		34.29	5.19	23.97	13.01	9.06
<i>IX</i>	C ₇ H ₉ Cl ₂ F ₆ N (292.1)	28.79	3.11	24.28	39.03	4.79
		29.37	3.14	23.44	38.58	5.09
<i>IV</i>	C ₈ H ₁₅ ClF ₃ N (217.7)	44.14	6.94	16.29	26.19	6.44
		43.88	6.72	16.00	26.61	6.23
<i>X</i>	C ₁₀ H ₁₅ Cl ₂ F ₆ N (334.2)	35.95	4.52	21.22	34.12	4.19
		36.26	4.70	21.06	33.88	4.17
<i>XIV</i>	C ₈ H ₁₆ F ₃ N (183.2)	52.44	8.82	—	31.10	7.64
		53.34	9.03	—	32.45	7.85

TABLE II
 Values of Proton Signals in PMR Spectra

Value of $\tau^{a,b}$	III^c	VII^d	IX^d	$XIII^e$	IV^c	X^c	XIV^d
H—CF	3.64 (2 dd)	3.37 (d)	3.61 (2 dd)	3.58 (2 m) 4.69 ^f (2 m)	3.54 (2 m)	3.65 (2 m)	4.53—5.33 (2 m) 5.47—6.22
N—CH ₃	7.65 (s)	6.76 (d) ^g 6.87 (d) ^h	7.38 (s)	7.61 (s)	—	—	—
N—CH—CF ₂	7.16 (td)	—	6.70 (td)	7.06 (t)	6.79 (m)	6.53 (m)	7.2 (m)
CH ₃ —CH	—	—	—	—	8.86 (d)	8.73 (d)	8.90 (d)
CH ₃ —CH ₂	—	—	—	—	9.00 (t) 7.51 (m)	8.95 (t) 7.33 (m)	9.01 (t) 7.57 (q)
² J _{HF}	48.00	50.5	48.5	48.0 44.0 ^f	46.0	49.0	—
³ J _{HF}	7 a 8 (13 ^e)	—	6 a 7 (14 ^e)	7 (12 ^e)	—	—	—
⁴ J _{HF}	2	—	1.5	—	—	—	—
J _{CH₃CH}	—	—	—	—	7.2	6.4	6.5
J _{CH₃CH₂}	—	—	—	—	7.2	7.0	7.0

^a The values are given in τ ; ^b the interaction constants are given in Hz; ^c measured on Tesla BS 478 (80 MHz) spectrometer in tetrachloromethane; ^d measured on Tesla BS 477 (60 MHz) spectrometer in deuteriochloroform; ^e in CF₂CH₂-N; ^f in —CHF—; ^g ⁵J_{CH₃-F} = 1.5 Hz; ^h ⁵J_{CH₃-F} = 0.8 Hz.

atom in the $-\text{CFCl}$ -grouping, relative to the CFClH group^{9,10}, the reduction of the chlorine atom in 1 : 2 telomer *XI* took place on $\text{C}_{(3)}$. The structure of amide *VII* was unequivocally assigned on the basis of IR and PMR spectra. Besides the doublet of proton in HCFI -group, the PMR spectrum shows two signals of methyl protons, each splitted into doublet by interaction with fluorine atom¹³. In the mass spectrum of the amide *VII* the molecular ion m/e 139 is accompanied by the ion m/e 141; their mutual ratio indicates that the compound contains one chlorine atom¹¹. The most important ion of the spectrum is that with m/e 72 ($(\text{M}-67)^+$), which is chlorine-unsubstituted. Other ions of interest are those with m/e 104($(\text{M}-\text{Cl})^+$), 44, and 42; the ion 58 does not appear.

It can be expected that the reaction products of the addition of triethylamine to trifluorochloroethylene will be a mixture of two or more diastereoisomeric racemates, depending on the number of chirality centers in the molecule. These racemates were for individual amines identified together by means of elemental analysis (Table I) and PMR spectra (Table II). The individual diastereoisomeric amines were separated by gas chromatography and then subjected to mass spectrometric analysis. Mass spectra of the diastereoisomers of the same structure were identical. For this reason the $-\text{CHClF}$ proton signal in their PMR spectra is referred to as the doublet of multiplets¹⁰, since we were unable to assign the signals to the individual diastereoisomeric racemates.

According to its mass spectrum, the 1 : 1 adduct *IV* has molecular weight 217 and contains one chlorine atom. The main ionic species of the spectrum is the ion m/e 100, other ions, listed in the order of decreasing intensity, being m/e 44, 72, 42, 56, 202 ($(\text{M}-15)^+$), 69, 174, 67, 182 ($(\text{M}-35)^+$), etc. The ion m/e 100 undergoes decomposition, giving the ion m/e 72 (confirmed by metastable ion) and this, along with the ions 44, 42, and 56¹², is in harmony with the suggested and by the PMR spectrum confirmed structure of the amine *IV* (Table II). In the mass spectrum of the 1 : 2 adduct *X* the molecular ion m/e 333 is accompanied by more intense ion $(\text{M}-1)^+$. The ratio of intensities of the ions $(\text{M}-15)^+$ of m/e 318 and 320 indicates that the compound contains two chlorine atoms¹¹. The most intense ionic species is the ion m/e 216 ($(\text{M}-117)^+$) which contains one chlorine atom, other important ions being m/e 218, 56, 42, 44, 188, 318, etc. The intensity of the other ions important for structure determination does not exceed several per cent. These are, e.g. the ions $(\text{M}-19)^+$, $(\text{M}-63)^+$ (formed from the ions $(\text{M}-35)^+ \rightarrow (\text{M}-63)^+ + 28$), $(\text{M}-47)^+$ (formed from the ions $(\text{M}-19)^+ \rightarrow (\text{M}-47)^+ + 28$), etc. The pattern of mass spectrum thus confirms the structure suggested for the amine *X* on the basis of PMR spectra (Table II). The mass spectrum of the isomeric 1 : 2 telomer *XII* resembles that of the amine *X*; the molecular ion m/e 333 is accompanied by more intense ion $(\text{M}-1)^+$ and the presence of two chlorine atoms is indicated by the ratio of intensities of the ions $(\text{M}-15)^+$ of m/e 318 and 320. In contradistinction to the amine *X*, the main ion is that of m/e 100, which is followed by the ions m/e 42, 44, 56, and 72, similarly as in the amine *IV*. The above data indicate that we deal here with the 1 : 2 telomer *XII*.

The structure of reduction products was mostly determined on the basis of analysis of their mass spectra. In the spectrum of the amine *XIV* we found the molecular ion m/e 183. The molecule does not contain chlorine. The most intense ion is m/e 100, followed by ions m/e 44, 42, 56, 72, 168 ($(\text{M}-15)^+$), 140, etc. The fragmentation of the $-\text{CF}_2\text{CH}_2\text{F}$ group gives rise to the ions $(\text{M}-19)^+$ and ion $(\text{M}-63)^+$ with low intensities. The latter is formed by the sequence $(\text{M}^+) \rightarrow (\text{M}-15)^+ \rightarrow (\text{M}-43)^+ \rightarrow (\text{M}-63)^+$ (confirmed by metastable ions). The structure of the amine *XIV* was also proved by PMR spectroscopy. The signal of CH_2F -protons lies at higher τ than

the CHClF proton of the amine *IV*, this being the result of reductive splitting-off of electronegative chlorine atom¹⁰. However, instead of the expected doublet of triplets they form the doublet of multiplets. As inferred from their mass spectra, the amines *XVI* and *XVII* are similar in structure with the amine *X*, differing from each other in number of chlorine atoms. Compound *XVI* has molecular ion *m/e* 299 (and contains one chlorine atom in the molecule¹¹). The most intense ion is *m/e* 216 ((M-83)⁺), followed by similarly intense ion 182 ((M-117)⁺) and by ions *m/e* 42, 44, 56, 186, 154, 284, 51, etc. Ion *m/e* 154 and 186 is formed from ion *m/e* 182 and 216, respectively, by loss of 28 mass units, similarly as in the case of the amine *XVII* and *X*. In the spectrum of amine *XVII* the molecular ion *m/e* 265 is accompanied by ion (M-1)⁺, both being of similar intensity. The compound does not contain chlorine and the most frequent ion of its spectrum is *m/e* 182 ((M-83)⁺). The fragment *m/e* 182 is probably analogous to the ion *m/e* 216 in the amine *X* where, however, one chlorine atom is replaced by hydrogen. The ion *m/e* 154 is formed from the ion *m/e* 182 by loss of 28 mass units (confirmed by metastable ion). The structure of amine *XV* was inferred from similarity of its mass spectrum with the spectrum of amine *XII*. By contrast to the amine *XII*, the amine *XV* contains only one chlorine atom. The molecular ion *m/e* 299 is accompanied by ion (M-1)⁺. The most intense ion is *m/e* 100, other important ions being *m/e* 42, 44, 46, 284, etc. The structure of amine *XV* follows from the higher reactivity of chlorine atoms in the —CFCl— grouping, relative to the —CFClH one¹⁰ and from analogy with amine *XIII*.

EXPERIMENTAL

The temperature data are uncorrected. The PMR spectra were recorded on Tesla BS 778 (80 MHz) and Tesla BS 477 (60 MHz) spectrometers in tetrachloromethane and deuteriochloroform, using tetramethylsilane and hexamethyldisiloxane as internal standards. The mass spectra were measured on Gas Chromatograph-Mass Spectrometer LKB 9000. The mass spectrometer was one-focusing with magnetic recording to the mass-scale. Ions are formed by electron impact (in recording the spectrum the energies of electrons were 70 eV) in the ion source heated to 290°C. The glass chromatographic column of the instrument was 2.3 mm across and 2.5 m long. Stationary phases were Carbowax 20 M and Apiezon L on Chromosorb and Celite, respectively; carrier gas was helium (more than 99% pure). On recording chromatographic spectra the energy of bombarding electrons was 20 eV. Gas chromatographic analyses were carried out on an instrument equipped with flame-ionization detector, the column diameter was 0.6 cm, stationary phase was 20% poly(propylene)succinate on Celite 545, carrier gas was nitrogen. Preparative gas chromatography was done in an apparatus not commercially available.

Addition of Trimethylamine to Trifluorochloroethylene Induced by γ -Irradiation (⁶⁰Co)

A glass ampoule was filled by condensation with 71.6 g (1.21 mol) of trimethylamine and 21.0 g (0.18 mol) of trifluorochloroethylene, sealed and irradiated at room temperature by a total of $5 \cdot 10^6$ r of γ -irradiation (⁶⁰Co). Then the ampoule was opened and the trimethylamine and traces of the unreacted olefin were removed by warming up the ampoule to 50–60°C. This was accompanied by a formation of water-soluble crystals on the walls of the ampoule. The determination of structure of the crystals was not attempted. Distillation of the reaction product yielded: 1. Fraction (20.8 g) of b.p. 118–125°C (33–35°C/13 Torr) which was chromatographically pure and was identified by elemental analysis (Table I), PMR (Table II) and mass spectra as the amine *III*; 2. Fraction (3.65 g) of b.p. 35–80°C/16 Torr, which, according to chromatographic analysis, consisted of amines *III* and *IX* (with the longest retention time). Chromatogram also showed the presence of small amounts of amine *XIII* and amide *VII*, the peaks of which were located between those of amines *III* and *IX*; 3. Distillation residue (1.7 g) which was not analysed. A mixture of compounds *IX*, *XIII* and *VII* was obtained by fractional distillation of the fractions of similar composition collected from two other runs carried out under identical conditions, and amine *IX* and amide *VII* were separated by preparative gas chromatography. The amine *XIII* was contaminated by c. 10% of amide *VII*. The products were identified by elemental analysis (Table I), PMR spectra (Table II), and mass spectra; in the case of amide *VII* its IR spectrum was also recorded (820 ms, 836 w, 982 ms, 1061 s, 1093 ms, 1150 w, 1191 w, 1247 ms, 1268 w,

1323 w, 1342 w, 1408 ms, 1418 ms, sh, 1460 w, 1503 ms, 1643 w, sh, 1680 vs, 1698 s, sh, 2815 vw, 2870 w, 2943 ms, 3015 vw, 3580 vw).

Addition of Triethylamine to Trifluorochloroethylene

1. *Initiation by UV light*: A glass reactor equipped with a reflux condenser, a frit for inlet of the olefin and a water-cooled mercury lamp Philips HPK 125 or Tesla RVK 125 W (silica filter) was filled with 150 ml (109.5 g) of triethylamine and then trifluoroethylene was being introduced in the rate of c. 2.5 l/h for 8.5 h. The temperature of the reaction mixture was maintained at 20–25°C by appropriate cooling the mercury lamp. In the course of the reaction water-soluble crystals began to precipitate on the inside walls of the silica filter; the aqueous solution gave positive test on chloride ions. By rectification of the liquid portion on a 20 cm Vigreux column the triethylamine was removed and 7 fractions were obtained. These were analyzed by gas chromatography. The content of individual components was determined by calculation from chromatograms of individual fractions. The 1:1 adduct *IV* and 1:2 adduct *X* were obtained practically pure. The first fraction and partly also the second fraction contained besides amine *IV* three other substances with a shorter retention time, the amine *XIV* prevailing. Analysis of the fourth fraction revealed besides amines *IV* (the shortest retention time) and *X* (the longest retention time) several substances which were separable only with difficulty. Therefore, they are

TABLE III
Results of Radical-Induced Addition of Triethylamine to Trifluorochloroethylene

Fraction °C/Torr	Weight g	Weight distribution, g				
		<i>XIV</i>	<i>IV</i>	<i>XII</i> + <i>XVI</i> ^a	<i>X</i>	not identified
Initiated by UV light						
64/15	3.20	0.54	2.43	—	—	0.23
64–66/15	15.30	0.92	13.92	—	—	0.46
66–68/15	17.70	—	17.70	—	—	—
69–120/15	6.70	—	1.27	1.41	4.02	—
121–124/15	5.40	—	0.10	0.92	4.38	—
125–126/15	12.30	—	—	0.98	11.32	—
80–84/0.6	7.15	—	—	0.15	7.0	—
Sum ^b		1.46	35.42	3.46	26.72	0.69
Initiated by γ -irradiation (⁶⁰ Co)						
75/18	4.70	—	4.70	—	—	—
75–127/17	1.40	—	0.30	0.10	1.00	—
127–130/17	2.6	—	0.04	0.08	2.48	—
Sum ^c			5.04	0.18	3.48	—

^a Present in trace amounts were *XV* and *XVII*; ^b distillation residue 14.40 g; ^c distillation residue 0.9 g.

treated as a whole in determining weight proportion in the individual fractions. Their complete separation was achieved on a gas chromatograph connected with mass spectrometer (Carbowax 20M). According to the mass spectra, this mixture consists predominantly of amine *XVI* and 1 : 2 telomer *XII* (in the ratio c. 2 : 1), amines *XV* and *XVII* being present in negligible amounts. The results are summarized in Table III.

2. *Initiation by γ -irradiation (^{60}Co)*: A glass ampoule was filled with 100 ml (72.9 g) of triethylamine, flushed with nitrogen, evacuated at water pump pressure, cooled with a dry ice-ethanol mixture and filled by condensation with 6 g of trifluorochloroethylene. The ampoule was then sealed and irradiated at room temperature with a total of $6 \cdot 10^6$ r of γ -irradiation (^{60}Co). It was then cooled in a mixture of dry ice with ethanol, opened and the content allowed to warm up to room temperature. Distillation of the product yielded three fractions. The main components of fractions were identified by chromatography, by comparing their retention times with those of standards. The results are presented in Table III.

Reduction of C—Cl Bonds by Triethylamine

The reduction of amine IV: A solution of 2.7 g of amine *IV* in 50 ml of triethylamine was irradiated under nitrogen atmosphere by a water-cooled, high-pressure mercury lamp Tesla RVK 125 for 29 hours, using the same apparatus as in the photochemical addition of triethylamine to trifluorochloroethylene. The reaction mixture was intermittently mixed up by a stream of nitrogen. During the reaction crystals were precipitating on the silica filter of the mercury lamp (probably triethylamine hydrochloride) which were always after c. 6 hours removed by washing the walls with water. The aqueous solution gave positive test on chloride ions. After the irradiation was completed, the filtrate was freed from triethylamine by distillation. Distillation of the residue afforded 1.2 g of the fraction, b.p. 40—42°C/13 Torr, from which the amine *XIV* was isolated by preparative gas chromatography. According to the gas chromatogram, the fraction contained in addition to amine *XIV* and the starting substance *IV* (in the ratio 95 : 5) three compounds with longer retention times, the structure of which was not determined.

The reduction of amine X: A solution of 3.1 g of amine *X* in 70 ml of triethylamine was irradiated under the conditions specified in the preceding paragraph for 20 hours. After filtering-off the crystals and removing the triethylamine by distillation, the fractionation of the residue yielded 1.6 g of the fraction, b.p. 80—95°C/9 Torr, which, according to chromatographic analysis, proved the conversion of the amine *X* into a mixture of amines *XVI* and *XVII*. The amines were identified only on the basis of the mass spectra recorded at the maximum of the chromatographic peak. Further fraction consisted of a mixture of products (0.8 g) boiling 115—150°C/9 Torr, the analysis of which was not attempted.

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