

Catalytic and Noncatalytic Ammonolysis of Chloropentafluorobenzene*

G. A. Selivanova, L. M. Pokrovskii, and V. D. Shteingarts

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,
pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia

Novosibirsk State University, Novosibirsk, Russia

Received July 10, 2000

Abstract—Ammonolysis of chloropentafluorobenzene both in the presence and in the absence of copper(I) salt results mainly in replacement of the *para*- and *ortho*-fluorine atoms with respect to chlorine rather than replacement of the chlorine atom. Ammonolysis of 4-chloro-2,3,5,6-tetrafluoroaniline and 2-chloro-3,4,5,6-tetrafluoroaniline in the absence of copper(I) salt yields exclusively the corresponding fluorine substitution products, whereas in the presence of copper(I) salt the chlorine atom is replaced. Successive ammonolysis of chloropentafluorobenzene in the presence of copper catalyst along these two paths was put into the basis of a new method for preparation of 2,3,5,6-tetrafluoro-1,4-phenylenediamine.

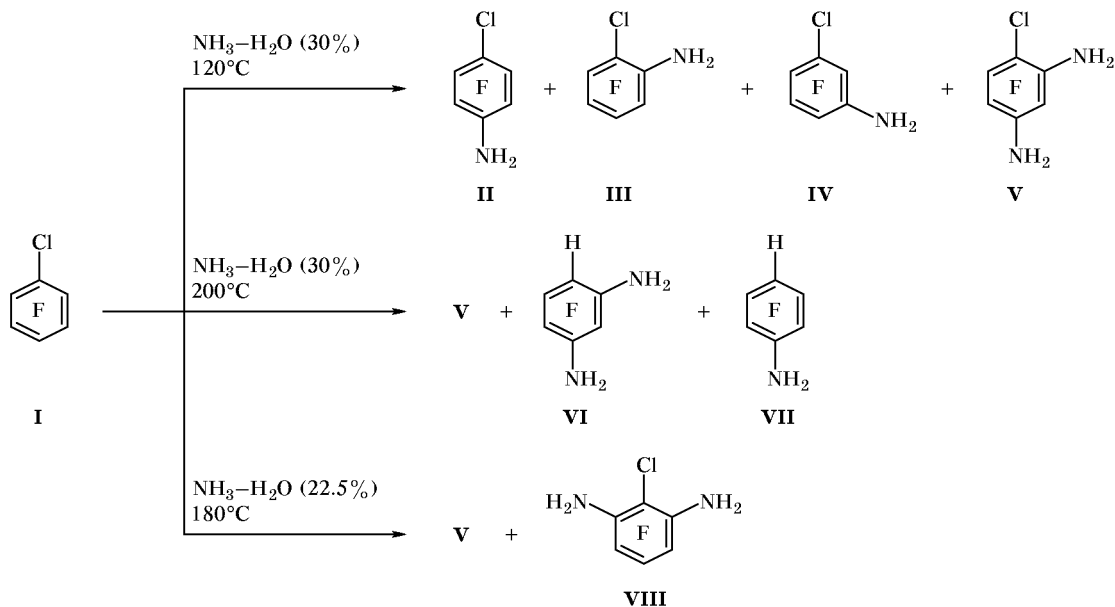
Polyfluorinated aromatic amines and diamines are often obtained by reactions of polyfluoroarenes with ammonia and amines. Numerous examples were reported on nucleophilic replacement of fluorine in polyfluoroarenes by amino group by the action of ammonia in water or aqueous ethanol [1–7]. It was found that in compounds containing both fluorine and other halogen atoms fluorine atoms are more reactive than chlorine [6] and bromine [1]. The ammonolysis of chloro- and bromopentafluorobenzene yields mainly the corresponding 4-halotetrafluoroanilines. Likewise, reactions of chloropentafluorobenzene (**I**) with hydrazine hydrate [6, 8], dimethylamine [9], and piperidine [10, 11], as well as reaction of bromopentafluorobenzene with hydrazine hydrate [9], gave with high yield products of fluorine replacement preferentially in the *para*-position relative to chlorine or bromine. We have found no examples of the reverse lability order of fluorine and heavier halogens in such reactions in the absence of a catalyst. However, reactions of chlorofluorobenzenes with aqueous ammonia in the presence of copper compounds [12] lead to the corresponding fluoroanilines as a result

of replacement of the chlorine atom. Until recently, the possibility for catalytic replacement by amino group of a non-fluorine halogen atom in polyfluoroaromatic compounds was questionable. Nevertheless, this problem is very important from the viewpoint of extending the scope of utilization of such accessible compounds as chloropolyfluorobenzenes [13]. The goal of the present work was to study ammonolysis of chloropentafluorobenzene (**I**) in the absence of a catalyst and in the presence of copper(I) salt. We also tried to elucidate the sequence of noncatalytic and catalytic transformations of primary substitution products under similar conditions. The reactions were carried out in a steel high-pressure reactor; the reaction time was 48 h. The reaction mixtures were analyzed by GLC and ¹⁹F NMR spectroscopy. The results are summarized in Table 1.

The reaction of chloropentafluorobenzene (**I**) with 30% aqueous ammonia at 120°C yields mainly 4-chloro-2,3,5,6-tetrafluoroaniline (**II**) and 2-chloro-3,4,5,6-tetrafluoroaniline (**III**) at a ratio of ~ 3:1 (run. no. 1, Scheme 1). These results coincide with published data on the ammonolysis of compound **I** in aqueous ethanol [6] and are consistent with those reported for reactions of **I** with other amines [9, 11]. The reaction mixture also contained small amounts (3–10%) of 3-chloro-2,4,5,6-tetrafluoroaniline (**IV**) and 4-chloro-2,5,6-trifluoro-1,3-phenylenediamine (**V**)

* This study was financially supported by the Russian Foundation for Basic Research (project no. 99-03-33111), by the Ministry of Science and Technology of the Russian Federation (project no 9.3.01), and by the Ministry of Education of the Russian Federation (project no. 015.05.01.13).

Scheme 1.



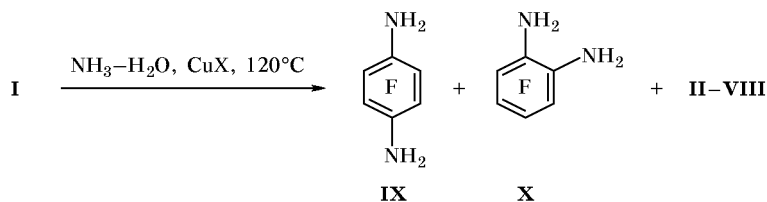
which is the product of further transformations of amines **II** and **III**.

In an attempt to obtain compound **V** as the major product we performed the reaction at higher temperature (200°C , run no. 2). In this case the major products were 2,5,6-trifluoro-1,3-phenylenediamine (**VI**) and 2,3,5,6-tetrafluoroaniline (**VII**), whereas the fraction of compound **V** in the mixture was as poor as 5%. The formation of diamine **VI** and amine **VII** may be regarded as analogous to some extent to the formation of pentafluorobenzene in the reduction of chloropentafluorobenzene (**I**) with copper in water at 300°C [14]. A question arises so as to whether replacement of fluorine in the initial substrate is followed by reductive dechlorination or the primary product is pentafluorobenzene which then undergoes ammonolysis. It should be emphasized that in our case the hydrodechlorination occurs under considerably milder conditions than those reported in [14]; presumably, the reactor material plays the role of reducing agent. The reason for the above difference may be the presence of

amino group in the substrate (if primary products of ammonolysis of **I** undergo reductive dechlorination) or the use of aqueous ammonia instead of water; both these call for additional investigation.

When the reaction was performed with aqueous ammonia of a lower concentration (22.5%, run no. 3) at 180°C , the major products were diamine **V** and 2-chloro-4,5,6-trifluoro-1,3-phenylenediamine (**VIII**) at a ratio of 14:1. Previously unknown compounds **V** and **VI** were isolated by recrystallization, and their structure was confirmed by the ^{19}F NMR and high-resolution mass spectra (see Experimental). The ^{19}F chemical shifts of compounds **V** and **VI** (Table 2) differ by no more than 1–2 ppm from those calculated by the additivity scheme using substituent increments from [15]; the corresponding differences for the other isomers containing three nonequivalent fluorine atoms are 4–8 ppm. The coupling constants given in Table 2 are also consistent with the proposed structures. The signal at $\delta \sim 6$ ppm in the ^1H NMR spectrum of **VI** is split due to coupling with fluorine atoms through

Scheme 2.



X = Cl, Br.

Table 1. Conditions and results of noncatalytic and catalytic ammonolysis of halogenated arenes **I–III**, **XI**, and **XIII** (48 h, 30% aqueous ammonia)

Run no.	Substrate (amount, g)	Reagent, ml	Substrate–CuX molar ratio	Temperature, °C	Yield, g	Product (fraction, mol %, GLC)
1	I (25)	180	–	120	21.4	II (70), III (22), IV (5), V (3)
2	I (11)	180	–	200	5.5	V (5), VI (71), VII (23)
3	I (10)	100 ^a	–	180	8.6	II (4), III (0.1), IV (1), V (83), VIII (6)
4	I (3)	60	1:1 (CuCl)	120	2.0	II (9.6), III (7.9), IV (2.2), V (4.4), VI (1.3), VII (8.8), VIII (1.2), IX (51.9), X (10.4)
5	I (3)	60	1:1 (CuBr)	120	2.0	II (0.2), III (3), IV (0.2), V (5.3), VI (2.1), VII (8.7), VIII (1.3), IX (55.8), X (17.8)
6	XI (3)	60	1:1 (CuCl)	120	2.5	XI (89), IX (1.5), XII (9.5)
7	XI (1)	60	–	120	0.7	XI (77.5), IX (3), XII (19.5)
8	II/III ^b	60	1:1 (CuCl)	120	2.0	II (0.2), III (2.4), IV (0.2), V (3.5), VI (3.8), VII (12.6), VIII (1.9), IX (55.5), X (15)
9	XIII (1) ^c	60	–	120	0.5	XIII (7), XV (39), XVI (19)
10	XIII (1) ^c	60	1:1 (CuCl)	125	1.0	VII (39), XIII (1.2), XV (15), XVI (13)

^a Aqueous ammonia (22.5%).

^b A mixture containing 63% of **II**, 20% of **III**, and 10% of **V** (GLC).

^c A mixture containing 74% of **XIII** and 11% of chloro-2,3,4,5-tetrafluorobenzene (**XIV**) (GLC).

the same constants as are the corresponding fluorine signals in the ¹⁹F NMR spectrum (Table 2).

Our results indicate that the ammonolysis of **I** in the absence of copper(I) salt involves exclusively replacement of fluorine. By contrast, the reaction of **I** with aqueous ammonia in the presence of copper(I) chloride or bromide (runs nos. 4 and 5; Scheme 2) afforded tetrafluoro-*p*- and -*o*-phenylenediamines **IX** and **X** as the major products together with amines **II–IV** and **VII** and diamines **V**, **VI**, and **VIII**. The results were the same regardless of whether copper(I) chloride or bromide was used.

The catalytic ammonolysis of compound **I** provides a new method for preparation of diamine **IX**. This procedure is superior to the known methods utilizing hexafluorobenzene as starting compound [13] (which can be regarded as equivalent to **I** in accessibility).

The known methods are characterized by approximately 3 times lower yield, and some procedures include a number of steps described in [2, 3, 16, 17]. Taking into account possible extensions of the developed approach to synthesis of polyfluorinated *p*-phenylenediamines, it was important to study the mechanism of ammonolysis of chloropentafluorobenzene (**I**) in the presence of copper(I) salts. The above results do not allow us to choose between two paths shown in Scheme 3, which differ by the order of replacement of fluorine and chlorine.

However, we believe that path *b* can be ruled out for the following reasons. First, even traces of amine **XI** were not detected among the products, although the conditions for catalytic ammonolysis of compound **I** (run no. 7) were milder than those reported in [2, 3] for complete transformation of **XI** into 2,4,5,6-tetrafluoro-1,3-phenylenediamine (**XII**) and diamine **IX** in the absence of copper salt. Second, in the latter case the major product was diamine **XII** (~90%) with a small impurity of isomer **IX**. The presence of copper ions could both accelerate the ammonolysis of **I** and change the reaction direction toward formation of diamine **IX**. However, by special experiment (run no. 6) we showed that the reaction direction does not change. On the other hand, path *a* is well consistent with the results of catalytic ammonolysis of a mixture

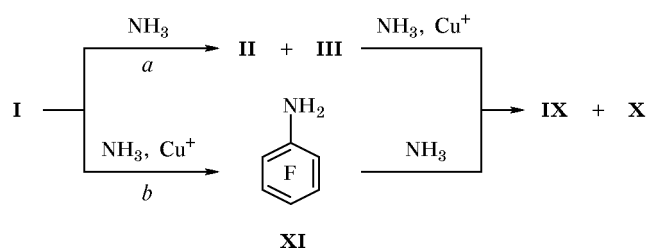
Scheme 3.

Table 2. ^1H and ^{19}F NMR spectra (δ and δ_{F} , ppm, J , Hz) of polyfluorinated aromatic amines (acetone- d_6 , 20%)

Comp. no.	^{19}F NMR spectrum ^a			^1H NMR spectrum
V	2-F, 5.2 [5.0], $J_{\text{F,F-}para} = 8$, $J_{\text{F,F-}meta} = 1.5$	5-F, 16.3 [17.0], $J_{\text{F,F-}ortho} = 22$, $J_{\text{F,F-}para} = 8$	6-F, -8.2 [-6.0], $J_{\text{F,F-}ortho} = 22$, $J_{\text{F,F-}meta} = 1.5$	4.92 (2H, NH_2), 4.77 (2H, NH_2)
VI	2-F, 3.2 [3.9], $J_{\text{F,F-}para} = 11$, $J_{\text{F,F-}meta} = 3$, $J_{\text{F,H-}meta} = 8$	5-F, 17.5 [19.7], $J_{\text{F,F-}ortho} = 22$, $J_{\text{F,F-}para} = 11$, $J_{\text{F,H-}ortho} = 12.5$	6-F, -9.3 [-14.3], $J_{\text{F,F-}ortho} = 22$, $J_{\text{F,F-}meta} = 3$, $J_{\text{F,H-}meta} = 8$	5.99 (H_{arom} , $J_{\text{F,H-}ortho} = 12.5$, $J_{\text{F,H-}meta} = 8$), 4.78 (2H, NH_2), 4.56 (2H, NH_2)
XV^b	3-F, 18.7 [17.5], $J_{\text{F,F-}ortho} = 21$, $J_{\text{F,F-}para} = 11$, $J_{\text{F,H-}meta} = 7$	4-F, 12.6 [13.7], $J_{\text{F,F-}ortho} = 21$, $J_{\text{F,F-}meta} = 4$, $J_{\text{F,H-}ortho} = 11$	6-F, 28.1 [25.2], $J_{\text{F,F-}para} = 11$, $J_{\text{F,F-}meta} = 4$, $J_{\text{F,H-}ortho} = 11$	6.80 (H_{arom} , $J_{\text{F,H-}ortho} = 11$, $J_{\text{F,H-}meta} = 7$), 4.78 (2H, NH_2)
XVI^b	2-F, 21.4 [20.4], $J_{\text{F,F-}para} = 11$, $J_{\text{F,F-}meta} = 7$, $J_{\text{F,H-}meta} \approx 8$	4-F, 8.8 [8.5], $J_{\text{F,F-}ortho} = 22$, $J_{\text{F,F-}meta} = 7$, $J_{\text{F,H-}meta} \approx 8$	5-F, 20.4 [22.0], $J_{\text{F,F-}ortho} = 22$, $J_{\text{F,F-}para} = 11$, $J_{\text{F,H-}ortho} \approx 12$	6.66 (H_{arom} , $J_{\text{F,H-}ortho} = 12.5$, $J_{\text{F,H-}meta} = 8$), 4.85 (2H, NH_2)

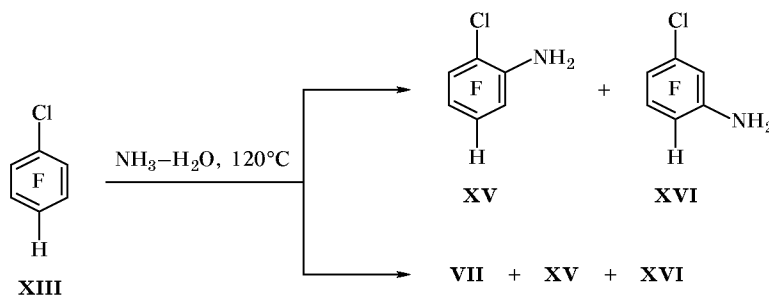
^a The values in brackets were calculated by the additivity scheme using the increments from [15].

^b The ^{19}F chemical shifts of amine **XI** [20] were used as increment for the amino group.

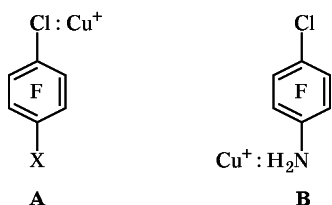
of anilines **II** and **III** (~3:1) (run no. 8), which was obtained by the reaction of **I** with ammonia in the absence of copper. The major products were amine **VII** and diamines **IX** and **X**, the ratio of the two latter being almost the same as in the products of catalytic ammonolysis of compound **I**.

Presumably, the relative rates of noncatalytic substitution of fluorine and catalytic substitution of chlorine depend on the presence of amino group in the substrate. In the ammonolysis of compound **I** both in the presence and in the absence of copper(I) salt replacement of fluorine in the *para*- and *ortho*-positions with respect to chlorine prevails over replacement of chlorine. The main direction of noncatalytic ammonolysis of amines **II** and **III** is also replacement of fluorine which occurs in the *meta*-position with

respect to the amino group, as in the case of pentafluoroaniline [2, 3]. By contrast, in the catalytic process substitution of the chlorine atom in **II** and **III** becomes the main reaction pathway. Probably, the presence of amino group favors catalytic replacement of chlorine in the *para*-position, which successfully competes with noncatalytic substitution of fluorine in the other positions. This assumption is supported by the results of ammonolysis of chloro-2,3,5,6-tetrafluorobenzene (**XIII**): the noncatalytic reaction, like with compound **I**, results in exclusive replacement of fluorine and formation (according to the ^{19}F NMR and GC-MS data) of isomeric chlorotrifluoroanilines **XV** and **XVI** (run no. 9), while the catalytic process (unlike the reaction with amines **II** and **III**) affords amine **VII** and a comparable amount of the fluorine

Scheme 4.

replacement products (run no. 10, Scheme 4). The assistance by amino group to aminodechlorination at the *para*- and *ortho*-positions in the catalytic reaction may be explained *a priori* by formation of two types of complexes between the substrate and copper(I) ion. In terms of the classical mechanism of catalysis by copper compounds as applied to ammonolysis of aryl halides [12], copper(I) ion coordinates at the halogen atom thus facilitating its elimination as halide ion. The presence of an amino group could increase the basicity (coordinating power) of the halogen. This means that replacement of $X = F$ or H by $X = NH_2$ could raise the equilibrium concentration of type **A** complex (see below). On the other hand, copper(I) ion could also coordinate at the amino group as the most basic center. As a result, the amino group should become electron-acceptor *para*(*ortho*)-orienting substituent, and in the corresponding type **B** complex the chlorine atom should readily be replaced.



Presumably, the mechanism of catalysis involving formation of complex **B** can be ruled out, for we observed no catalytic effect of copper in the ammonolysis of compound **XI**. Another reason is that no fluorine replacement occurred at the *ortho*-position with respect to the amino group in amine **II** and at the *para*-position in amines **III**, **XV**, and **XVI**.

EXPERIMENTAL

The 1H and ^{19}F NMR spectra of 20% solutions in acetone- d_6 were recorded on Bruker WP-200 and Bruker AM-400 spectrometers relative to HMDS and C_6F_6 , respectively, as internal references. The reaction mixtures were analyzed by GLC on a Hewlett-Packard HP 5890 chromatograph equipped with a thermal conductivity detector; injector temperature 200°C; detector temperature 240°C; oven temperature programming from 40°C (1 min) to 240°C at a rate of 10 deg/min; HP-5 capillary column (polymethylphenylsilicone), 151000 × 0.53 mm, film thickness 1.5 μm ; carrier gas helium, 5 ml/min. The components were quantitated by the internal normalization technique.

The high-resolution mass spectra were obtained on a Finnigan MAT-8200 mass spectrometer. The

products were identified by GC-MS using a Hewlett-Packard G1081A system consisting of an HP 5890 Series II gas chromatograph and HP 5971 mass-selective detector; energy of ionizing electrons 70 eV; oven temperature programming from 50°C (2 min) at 10 deg/min to 280°C (5 min); injector temperature 280°C; ion source temperature 173°C; HP-5 capillary column, 30 m × 0.25 mm × 0.25 μm ; carrier gas helium, 1 ml/min; data acquisition at 1.2 scan/s, mass range 30–650 amu.

Commercial chloropentafluorobenzene (**I**), 1,4-diamino-2,3,5,6-tetrafluorobenzene (**XI**), and aqueous ammonia were used. The latter was saturated with gaseous ammonia to attain a concentration of 30% (d 0.893 g/cm³). Compound **XIII** was a mixture with isomeric 2,3,4,5-tetrafluorochlorobenzene (**XIV**) at a ratio of 7:1; it was synthesized by reaction of **I** with hydrazine hydrate according to the procedure reported in [6] and subsequent oxidation of the hydrazo derivatives [18]. The spectral parameters of previously known compounds were in agreement with published data [2, 16, 18–21]. Table 2 contains the 1H and ^{19}F NMR spectral data of newly synthesized compounds **V**, **VI**, **XV**, and **XVI**.

Typical procedure for reaction of polyfluoroaromatic compounds with aqueous ammonia.

A steel rotating high-pressure reactor was charged with polyhalogenated benzene, aqueous ammonia, and copper halide (in the catalytic process), and the reactor was rotated for 48 h at 120°C. The mixture was cooled, transferred into a flask, and steam-distilled. The distillate was extracted with diethyl ether, the extract was dried and evaporated, and the residue was analyzed by GLC (Table 1).

2,3,5,6-Tetrafluoro-1,4-phenylenediamine (**IX**).

The reaction mixture obtained by the above procedure from 40 g of chloropentafluorobenzene and 720 ml of 30% aqueous ammonia was steam-distilled. A fraction was collected until crystals appeared in the distillate. It was extracted with diethyl ether (3 × 50 ml) to obtain 4.2 g of a solid product containing (GLC) 1.8 g of compound **VII**, 0.9 g of amine **III**, 0.4 g of diamine **IX**, and 0.1 g of diamine **X**. From the next portion of the distillate 16 g of a solid material was filtered off. Extraction of the filtrate with diethyl ether gave an additional 3.1 g of a solid product which was combined with the major portion. According to the GLC data, the product contained 14.4 g of diamine **IX** and 1.9 g of **X**. By recrystallization from petroleum ether (bp 70–100°C) we isolated 9 g (38%) of 2,3,5,6-tetrafluoro-1,4-phenylenediamine containing 97% of the main substance, mp 142–144°C [2].

6-Chloro-2,4,5-trifluoro-1,3-phenylenediamine (V) was synthesized by the general procedure from 20 g (~0.1 mol) of chloropentafluorobenzene and 200 ml of aqueous ammonia ($d = 0.915 \text{ g/cm}^3$, 2.37 mol). The mixture was treated as described above and was subjected to steam distillation for 30 min to remove volatile components. The still residue was cooled to 18–20°C, and the precipitate was filtered off. We isolated 18.5 g of dark needles containing (GLC) 86% of diamine **V** and 6% of diamine **VIII**. Recrystallization from petroleum ether (bp 70–100°C) gave 11 g of diamine **V** (purity 91%, yield 56%); the second recrystallization gave 5.8 g of compound **V** containing 97% of the main substance (yield 30%), mp 133.5–134.5°C. Found: M^+ 196.0016. $\text{C}_6\text{H}_4\text{ClF}_3\text{N}_2$. Calculated: M 196.0015.

2,4,5-Trifluoro-1,3-phenylenediamine (VI) was obtained by the general procedure (run no. 2, Table 1). Double recrystallization from petroleum ether (bp 70–100°C) gave 2.5 g of diamine **VI** containing 97% of the main substance (yield 24%), mp 68–68.5°C. Found: M^+ 162.0402. $\text{C}_6\text{H}_3\text{F}_3\text{N}_2$. Calculated: M 162.0405.

The authors are grateful to the staff of the Autoclave Department at the Novosibirsk Institute of Organic Chemistry for their assistance in carrying out experiments.

REFERENCES

- Wall, L.A., Pummer, W.J., Fearn, J.E., and Antonucci, J.M., *J. Res. NBS, Ser. A*, 1963, vol. 67, pp. 481–497.
- Brooke, G.M., Burdon, J., Stacey, M., and Tatlow, J.C., *J. Chem. Soc.*, 1960, no. 4, pp. 1768–1771.
- Yakobson, G.G., Shteingarts, V.D., Furin, G.G., and Vorozhtsov, N.N., Jr., *Zh. Obshch. Khim.*, 1964, vol. 34, no. 10, p. 3514.
- Sintezy ftorganicheskikh soedinenii* (Syntheses of Organofluorine Compounds), Knunyants, I.L. and Yakobson, G.G., Ed., Moscow: Khimiya, 1973, p. 192.
- Shtark, A.A., Chuikova, T.V., Selivanova, G.A., and Shteingarts, V.D., *Zh. Org. Khim.*, 1987, vol. 23, no. 12, pp. 2574–2580.
- Brooke, G.M., Chambers, R.D., Heyes, J., and Musgrave, W.K.R., *Proc. Chem. Soc.*, 1963, p. 213.
- Yakobson, G.G., Kobrina, L.S., Rubina, T.D., and Vorozhtsov, N.N., Jr., *Zh. Obshch. Khim.*, 1963, vol. 33, no. 4, pp. 1273–1277.
- Ichiakawa, N. and Hayashi, S., *Nippon Kagaku Zasshi*, 1968, vol. 89, no. 3, p. 321; *Chem. Abstr.*, 1968, vol. 69, p. 67021.
- Burdon, J., Coe, P.L., Marsh, C.R., and Tatlow, J.C., *Tetrahedron*, 1966, vol. 22, pp. 1183–1188.
- Holl. Patent 6611766, 1967; UK Patent 1161491, 1966.
- Bellas, M., Prince, D., and Suschitzky, H., *J. Chem. Soc. C.*, 1967, no. 13, pp. 1249–1254.
- Vorozhtsov, N.N., Yakobson, G.G., and Rubina, T.D., *Dokl. Akad. Nauk SSSR*, 1959, vol. 127, no. 6, pp. 1225–1227.
- Vorozhtsov, N.N., Platonov, V.E., and Yakobson, G.G., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1963, p. 1524; Yakobson, G.G., Platonov, V.E., and Vorozhtsov, N.N., Jr., *Zh. Obshch. Khim.*, 1965, vol. 35, no. 7, pp. 1158–1161.
- Sokolenko, V.I., L'vova, A.Ya., Tyurin, V.S., Platonov, V.E., and Yakobson, G.G., *Zh. Org. Khim.*, 1970, vol. 6, no. 12, pp. 2496–2498.
- Emsley, J.W., Feeney, J., and Sutcliffe, L.H., *High-Resolution Nuclear Magnetic Resonance Spectroscopy*, Oxford: Pergamon, 1966, vol. 2. Translated under the title *Spektroskopiya YaMR vysokogo razresheniya*, Moscow: Mir, 1969, vol. 2, p. 220.
- Forbes, E.J., Richardson, R.D., and Tatlow, J.C., *Chem. Ind.*, 1958, p. 630; Brooke, G.M., Burdon, J., and Tatlow, J.C., *J. Chem. Soc.*, 1961, no. 3, pp. 802–807; Shtark, A.A., Chuikova, T.V., and Shteingarts, V.D., USSR Inventor's Certificate no. 936612; *Byull. Izobret.*, 1983, no. 3.
- Holland, D.G., Moore, G.J., and Tamborski, C., *Chem. Ind.*, 1964, vol. 31, no. 6, pp. 1562–1565; Holland, D.G., Moore, G.J., and Tamborski, C., *Chem. Ind.*, 1965, vol. 31, pp. 376–377.
- Birchall, J.M., Haszeldine, R.N., and Parkinson, A.R., *J. Chem. Soc.*, 1962, no. 12, pp. 4966–4976.
- Homer, J. and Thomas, L.F., *J. Chem. Soc. B*, 1966, pp. 141–144.
- Lawrenson, I.J., *J. Chem. Soc.*, 1965, pp. 1117–1120.
- Bladon, P., Sharp, D.W.A., and Winfield, J.M., *Spectrochim. Acta*, 1964, vol. 20, pp. 1033–1042.