POLYFLUORINATION OF CYCLOHEXADIENONE COMMUNICATION 1. RADICAL CHARACTER OF TRANSFORMATIONS OF NITROCYCLOHEXADIENONES (QUINNITROLS) IN NEUTRAL MEDIA*

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It has been found that perfluoroaromatic compounds can take part in electrophilic addition reactions [1-5]. In this connection, polyfluorinated nitrocyclohexadienones (quinnitrols) are of interest as compounds modelling the properties of intermediate products of the above reactions. In particular, it can be assumed that in view of the similarity of electronic sheaths the properties of group $-CFNO_2-$ in quinnitrols (A) and σ -complexes (B) should be similar



Most of the transformations of polyfluoroquinnitrols, and quinnitrols as well, are connected with the disruption of the C-N bond [3, 6-8]. It has been shown in [6] that reaction of 2, 4, 6-tri-tert-butylphenoxyl with nitrogen dioxide leads to the formation of the corresponding quinnitrol; it has been postulated that the latter can undergo a reverse homolytic decomposition. Ley and Müller [7] assumed that in acidic media the decomposition of alkylated quinnitrols involves an ionic mechanism with the formation of anion NO_2 and cation ArO^+ .

There is no information in the literature about the character of the disruption of C-N bonds in reactions of quinnitrols containing group-CHalNO₂-. However, the transformation of 4-nitropentafluorocyclodien-2, 5-one-1 (I) into 4-(pentafluorophenoxy)pentafluorocyclohexadien-2, 5-one-1 (II) by reaction with pentafluorophenol, disclosed by us earlier [3], indirectly indicates a radical character of the decomposition of (I) with the formation of pentafluorophenoxy radical, because compounds similar to (II) are typical products of the dimerization of phenoxy radicals [9].

In the present work, we have obtained data corroborating the homolytic character of the disruption of the C-N bond in polyfluorinated quinnitrols during their decomposition in neutral media. These compounds are formed by the action of nitric acid on polyfluorinated phenols and naphthols [2-4], and on octafluoronaphthalene [2].

The reaction of quinnitrol (I) with phenol in dioxane leads to the formation, apart from pentafluorophenol, of o- and p-nitrophenols in approximately equal amounts. If under conditions of this reaction (I) decomposed to NO_2^- and $C_6F_5O^+$ (cf. [7]), the formation of nitrophenols should be preceded by nitrosation of phenol. However, it is well known that the nitrosation of phenol results practically exclusively in the formation of p-nitrosophenol, which can be oxidized further to p-nitrophenol [10]. When we have effected the reaction of phenol with nitrous acid in dioxane, we found in the reaction products p-nitrophenol only.

*On the basis of the decision of the Conference of Chief Editors of the journals of Academy of Sciences of the USSR (July 12, 1962), the present communication is published as Dissertation of A. G. Budnik.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2485-2492, November 1969. Original article submitted December 23, 1968.

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The formation of approximately equal amounts of o- and p-nitrophenols by reaction of (I) with phenol indicates that during the decomposition of (I) nitrogen dioxide or nitronium cations can be split off. In order to settle this question, we have carried out the decomposition of (I) in the presence of butadiene-1, 3 (III) and 2,3-dimethylbutadiene-1,3 (IV), which are known to combine with phenoxy radicals [11].

From the reaction products of (I) and (IV), we separated (II), 1, 4-dinitro-2, 3-dimethylbutene-2 (V) (which was earlier described as the product of the addition of NO₂ to (IV) [12], and also a compound of the composition $C_{18}H_{10}F_{10}O_2$ (VI), corresponding to the addition of two pentafluorophenoxyl residues to (IV). IR spectrum of (VI) comprises absorption bands at 1525 (fluorinated aromatic ring [13]), 1695 (C = O) and 1735 cm⁻¹ (CF = CF [14]). Thus, it can be assumed that a molecule of compound (VI) contains a pentafluorophenoxy fragment and pentafluorocyclohexadienone fragment. Correspondingly, the NMR F¹⁹ spectrum of the adduct of (VI) (Fig. 1) comprises signals at 0, -6, and -12 ppm* (2:1:2; the fine structure corresponds to that expected of the signals of fluorine atoms of pentafluorophenyl ring [15]), and also signals of an equal intensity at +17, -11, -14, -30, and -37 ppm (fluorine atoms of the dienone ring). UV spectrum of the adduct (VI) ($\lambda_{max} = 232 \text{ m}\mu$) is contradictory to the proposed structure of cyclohexadien-2,4-one-1 [16]. Nonequivalence of the five fluorine atoms indicates the rigidity of the conformation of adduct (VI) which inhibits a free rotation around the bond linking the cyclohexadienone fragment with the remaining part of the molecule. Consequently, of the five fluorine atoms only two are really free (at -37 and -14 ppm); the character of the splitting of these signals allows us to conclude that they are due to F atoms positioned at one double bond (cf. [17]).

Results of ozonizing indicate that compound (VI) is a product of 1,2-addition. During a reductive splitting of the ozonide with trimethyl phosphite, formaldehyde and ketone (VII) were separated. This corresponds to the replacement of one fluorine atom by methoxy group in the dienone fragment of the remaining part of the adduct molecule (VI) (according to the NMR F¹⁹ spectrum of dinitrophenylhydrazone, cf. [18]). Assumption of 1, 4-addition mechanism being in play must be rejected because of the absence in the ozonization products of pentafluophenoxyacetone, which was obtained by us by reaction between sodium pentafluorophenolate and bromoacetone.

All these results, in combination with a model analysis according to Stuart and Briegleb, indicate that the structure (VI) is more probable than its 1, 2-addition isomer in which the positioning of the phenyl and the cyclohexadiene fragment is reversed. On the basis of the assumption of the initial decomposition of quinnitrol (I) into pentafluorophenoxy radical and NO_2 , its reaction with diene (IV) can be represented by the following scheme



From the reaction products of quinnitrol (I) and diene (III) there were separated dimer (II) and a compound for which we propose (on the basis of spectral data) an adduct structure (VIII). The presence of a terminal double bond in this compound was proved by the formation of formaldehyde when the compound was subjected to ozonization.

We have also investigated the reaction between diene (IV) and compound (IX) formed by the action of nitric acid (sp. gr. 1.51) on tetrafluoro-p-cresol at -30 to -20 °C. We could not analyze this compound, because it intensively decomposes even at 30°; this decomposition proceeds in the same way as that of quinnitrol (I) [3]. By analogy with the formation of p-quinnitrols by the action of HNO₃ on tetrahalogeno-p-cresols [19], we propose for compound (IX) the structure of 4-nitro-4-methyltetrafluoro-cyclohexadien-2, 5-one-1. This assumption is in accordance with the presence of two signals of equal intensity at -14 and -42 ppm in

*Here, and hereinafter, with respect to the signal of hexafluorobenzene.



Fig. 1. NMR F¹⁹ spectrum of the adduct of (VI) (Varian A-56/ 60A; 56.4 MHz; 30% solution in acetone).

the NMR F^{19} spectrum of mixture obtained by dissolving tetrafluoro-p-cresol in HNO₃ at -30°. Compound (IX), while decomposing in the presence of diene (IV) gives adduct (X) which, according to UV and NMR spectra, is analogous to adduct (VI).

From the products of the reaction of 1-keto-4-nitroheptafluoro-1, 4-dihydronaphthalene (XII) with dienes (III) and (IV), we were able to separate, apart from a mixture of 1, 2- and 1, 4-hexafluoronaphthoquinones, only 1-keto-4-(heptafluoronaphthoxy-1')-pentafluoro-1, 4-dihydronaphthalene, the dimer of heptafluoro- α -naphthoxyl radical (XIII). The latter was also obtained by us by oxidation of heptafluoro- α -naphthol with lead peroxide. The structure of compound (XIII) was confirmed by IR, UV, and NMR spectra. Its IR spectrum comprises absorption bands at 1320 (Ar-O), 1500 and 1630 (fluorinated aromatic ring), 1665 (fluorinated naphthalene nucleus [13]), 1720 (C=O), and 1735 cm⁻¹ (CF=CF). The UV spectrum comprises $\lambda_{max_1} = 218 \text{ m}\mu$ (log $\varepsilon = 4.800$) and $\lambda_{max_2} = 282 \text{ m}\mu$ (log $\varepsilon = 3.938$). In the NMR F¹⁹ spectrum there is a multiplet at -58 ppm, having a relative intensity of 1 (fluorine atom attached to a saturated carbon atom [5]), and a group of signals having a total relative intensity of 13 in the range between -8 and -30 ppm (ole-finic and aromatic fluorine atoms).

The formation of the diene addition products of two polyfluorophenoxy residues, two NO_2 particles, and also dimers (II) and (XIII) supports the assumption about the homolytic character of the disruption of bond C-N in polyfluorinated quinnitrols. It would be very difficult to explain these results otherwise.

Assuming the radical character of the C-N bond disruption, the known transformation of polyhalogenated quinnitrols into polyhalogenoquinones [2,3,8] can be represented by the following scheme (cf. [20]):



According to this scheme, the reaction proceeds also in the absence of atmospheric oxygen, and the main component of the gaseous reaction products is nitrosyl fluoride. In an analogous manner, hexachlo-ronaphthoquinone-1, 4 and nitrosyl chloride are formed by thermolysis of 1-keto-4-nitroheptachloro-1, 4-dihydronaphthalene (XIV) both in the absence of atmospheric oxygen and under normal conditions [4]. If during the decomposition of quinnitrol (I) in dioxane or nitromethane NO_2 is partly removed by passing a strong stream of nitrogen, (II) is formed besides isomers of tetrafluorobenzoquinone. This does not occur when (I) is decomposed under normal conditions.

The question why polyfluorinated quinnitrols yield during decomposition mixtures of isomeric quinones, whilst perchlorinated quinnitrol (XIV) gives p-quinone only, is apparently connected with a small difference in the reactivity of polyfluorinated and polychlorinated aroxy radicals. The readiness of these and other transformations of quinnitrols is apparently connected with a relative stability of the aroxy radicals formed

by the homolytic disruption of the C-N bond, due to the resonance delocalization of the density of the unpaired electron.

It is known that the easy transformation of the $-CHalNO_2$ -fragment located in the position of "active" methylenic group into the carbonyl group has a fairly general character [5, 21]. We suppose that in all these cases such a transformation occurs by a radical mechanism analogous to that described above for the transformation of quinnitrols into quinones, due to the resonance stabilization of the radicals formed in the course of this process.

EXPERIMENTAL

Reaction of Quinnitrol (I) with Phenol. To a solution of 3 g of phenol in 25 ml of dioxane at 20° were added portionwise over 30 min (with stirring) 5 g of (I) prepared by the method described in [3]. After 3 h, the reaction mixture was poured into 300 ml of water and extracted with ether. This extract was dried over MgSO₄, and the solvent was evaporated. The residue was distilled under vacuum and the following fractions were collected: I at $45-47^{\circ}$ (5 mm), weight 4.4 g; and II at $62-65^{\circ}$ (5mm) weight 0.6 g. According to gas – liquid chromatography (silicone SKTNF; brick INZ-600; temp. 160°; flow rate 3.3 liters per hour; in helium) and IR spectroscopy, fraction I contained 52-55% of pentafluorophenol, 18-20% of phenol, and 6-8% of o-nitrophenol. Fraction II was a practically pure o-nitrophenol (according to IR spectroscopy); mp 44-45° (from petroleum ether). The still residue was recrystallized from water yielding 0.8 g of p-nitrophenol mp $113-114^{\circ}$.

<u>Reaction of Quinnitrol (I) with 2,3-Dimethylbutadiene-1,3.</u> Twenty grains of (I) were dissolved in 120 ml of benzene cooled to 8°, and 20 g of anhydrous Na₂SO₄ were added, followed by 7.3 g of (IV), with stirring. The stirring was continued for 40 min at 25-30°, then the mixture was filtered, and the solvent was evaporated under vacuum. The residue was distilled under vacuum, and the following fractions were collected: I at 75-115° (2 mm) weight 4.5 g; and II at 115-131° (2 mm), weight 11 g. A second distillation of fraction I gave 3.5 g of a yellow oil (bp 77-79° at 1 mm) containing according to gas-liquid chromatography (silicone SKTNF; brick INZ-600; temp. 140°; flow rate 3 liters per hour; in helium) 92% of (II), 20% with respect to compound (I). The IR spectrum of this product was close to the spectrum of pure (II). Fraction II was kept at 5° until crystals precipitated, which were separated by filtration and washed with cold methanol. The yield of adduct (VI) was 3.6 g (19%); mp 103-104° (from hexane). Found C 48.32, 48.51; H 2.34, 2.38; F 42.35, 42.59%; mol. wt. 447 ± 3 (by mass spectrometry). $C_{18}H_{10}F_{10}O_2$. Calculated: C 48.21; H 2.23; F 42.41%, mol. wt. 448.

The mother liquor from fraction II was again distilled under vacuum. A fraction boiling at $110-120^{\circ}$ (1.5 mm) was collected, cooled and kept at 0° for a prolonged period of time; 1.5 g (42%) of (V) was separated; mp 71-72° (from CCl₄); (according to [22] 71-71.5°).

When (I) was reacted with a 2-3-fold excess of (IV), the yield of (VI) increased to 35% whilst the yield of (II) decreased correspondingly.

Reaction of Quinnitrol (I) with Butadiene-1,3. Reaction of 25 g of quinnitrol (I) with 15 g of (III) was carried out in an analogous manner. After the evaporation of benzene, the residue was extracted with boiling heptane. The heptane was then evaporated from the extract, and the residue was distilled under vacuum; the following fractions were collected: I at 72-86° (1 mm), weight 3.2 g; and II at 86-99° (1 mm), weight 19.1 g. According to gas-liquid chromatography, fraction I contained 88% of (II), 14% with respect to (I). Fraction II was kept at 0° until crystals precipitated, which were triturated with a small amount of cold hexane; 9.8 g (42%) of (VII) were separated by filtration; mp 76-77° (from hexane). Found: C 45.71, 45.80; H 1.45, 1.55; F 44.79, 44.90% mol. wt. 414, 418 (by isothermal distillation). $C_{16}H_6F_{10}O_2$. Calculated: C 45.75; H. 1.43; F 45.25%; mol. wt. 420. IR spectrum (in CCl₄): 1520 (fluorinated aromatic ring), 1750 (C = O), 1790 cm⁻¹ (CF = CF). UV spectrum (in heptane): 222 m μ (log ε = 3.518). NMR F¹⁹ spectrum (in CCl₄): eight signals (intensities 1:1:2:1:2:1:1:1) at 38, 36, 0, -6, -10.5, -11, -15, and -34 ppm. Signals at 0, -6, and -10.5 ppm (2:1:2) related to the fluorine atom of pentafluorophenoxyl ring, and the remaining to the fluorine atoms of the cyclohexadienone ring.

<u>Tetrafluoro-p-Cresol.</u> 20 g of pentafluorotoluene and a solution of 20 g KOH in 180 ml water were stirred together in an autoclave for 16 h at 180-190°. The reaction mixture was acidified and extracted with ether. The extract was dried over MgSO₄, and ether was evaporated. The residue was distilled under vacuum yielding 14.5 g (23%) of tetrafluoro-p-cresol; bp 101-102° (60 mm); mp 52° (from petroleum ether); (according to [23] mp 52°).

<u>Reaction of Tetrafluoro-p-cresol with Nitric Acid.</u> Ten grams of tetrafluoro-p-cresol were added with stirring to 30 ml of nitric acid (sp. gr. 1.51) at a temperature not exceeding -20° . After 5 min, the solution was poured onto ice; the precipitate of quinnitrol (IX) was separated by filtration, washed with ice water, rapidly squeezed out, and dried over P_2O_5 at a temperature not exceeding 0° .

<u>Reaction of Quinnitrol (IX) with 2, 3-Dimethylbutadiene-1, 3.</u> Quinnitrol (IX) produced from 10 g of tetrafluoro-p-cresol was dissolved at 0° in 130 ml of a 3:1 mixture of benzene and hexane; then 20 g of anhydrous Na₂SO₄ and 11 g of (IV) were added. The cooling was discontinued, and the mixture was stirred for a further 20 min. The solution was filtered, and the solvent was evaporated under vacuum. From the residue, the fraction boiling to 90° at 1 mm was separated; and the still residue was extracted with heptane. After the removal of heptane, the residual extract was passed through a column containing 300 g of Al₂O₃ (pH 4), in the system benzene-hexane (1:8), whereby 3.5 g (40%) of the adduct (X) were obtained, mp 105-106° (from hexane). Found: C 54.33, 54.62; H 3.65, 3.73; F 34.65, 34.82%; mol. wt. 437, 442 (isotherm. dist.). C₂₀H₁₆F₈O₂. Calculated: C54.54; H 3.64; F 34.54%; mol. wt. 440. IR spectrum (in CCl₄): 1500 (fluorinated aromatic ring), 1680 (C=O), 1730 cm⁻¹ (CF=CF). UV spectrum (in heptane): 244 m μ (log ε = 4.064). NMR F¹⁹ spectrum (in acetone): six signals (intensity ratio $\frac{1}{2}$: 1: 2: 2: 1: 1) at 12, -4, -10, -20, -34, and -47 ppm. The signals at -10 and -20 ppm were due to the fluorine atoms of the aromatic ring; the remaining signals related to the fluorine atoms of the cyclohexadienone ring.

<u>Reaction of Quinnitrol (XII) with 2, 3-Dimethylbutadiene-1, 3</u>. To a solution of 20 g of (XII) (produced according to [2]) in 120 ml of abs. ether were added with stirring 5.8 g of (IV) at 20°. After 2 h, the solvent was evaporated under vacuum, and the residue was triturated with a small amount of ether; 1 g of a mixture of hexafluoronaphthaquinones (according to IR spectroscopy) was filtered off. From the filtrate, ether was evaporated and the residue was kept for one day at 0-5°. The crystallized precipitate was triturated with a small amount of cold methanol and filtered. The yield of (XIII) was 4.2 g (24%); mp 97-98° (from a heptane – CCl₄ mixture). Found: C 44.63, 44.83; F 49.43, 49.51%; mol. wt. 552, 561 (isotherm. dist.) C₂₀F₁₄O₂. Calculated: C 44.61; F 49.43%; mol. wt. 538.

Ozonization of Adducts (VI) and (X). Through a solution of 3 g of (VI) in a mixture of 30 ml CH_2Cl_2 and 100 ml abs. methanol at -60 to -40° was passed a stream of oxygen containing 1% of ozone. The ozonizing was terminated when the solution became blue colored, and nitrogen was blown through the reaction mixture for 5 min. At -60°, 3 ml of trimethyl phosphite were added, and the mixture was left overnight at 20°. The solution was divided into two equal parts, and one of them was steam-distilled. To the distillate, an excess of a dimedon solution was added and the mixture was left overnight. Then the remaining CH_2Cl_2 was evaporated under vacuum. The residue was filtered, washed with methanol and dried; 0.32 g (33%) of formaldimedon was obtained; mp 189-191° (from methanol). A sample mixed with a known specimen did not cause any depression of the melting temperature.

From the other portion of the solution, 2, 4-dinitrophenylhydrazone of ketone (VII) was produced by the the method described in [24]. It was purified by passing it through 300 g of acidic Al_2O_3 in the system benzene-chloroform (7:3); the yield was 0.9 g (40%); mp 209-211 (from a methanol-benzene mixture). Found: C 44.89, 44.95; H 2.39, 2.45; F 26.92, 27.03; N 8.36, 8.41; OCH₃ 4.52, 4.54%; mol. wt. 653, 658 (isotherm. dist.). $\dot{C}_{24}H_{15}F_9O_7N_4$. Calculated: C 44.86; h 2.34; F 26.63; N 8.72; OCH₃ 4.83%; mol. wt. 642.

In an analogous manner, ozonization of 2 g of adduct (X) yielded formaldimedon (48%) and 0.6 g (42%) of 2, 4-dinitrophenylhydrazone of ketone (XI); mp 223-225 (from benzene). Found: C 49.40, 49.52; H 3.38, 3.50; F 20.32, 20.41; N 8.44, 8.50; OCH₃ 5.15, 5.21% mol. wt. 656, 670 (isotherm. dist.): $C_{26}H_{21}F_7O_7N_4$. Calculated: C 49.21; H 3.32; F 20.97; N 8.84; OCH₃ 4.89%; mol. wt. 634.

<u>Pentafluorophenoxyacetone</u>. To a suspension of 7 g of pentafluorophenolate in 60 ml of abs. benzene were added 5 ml of bromoacetone, and the mixture was boiled with stirring for 3 h. The precipitate was filtered off; from the filtrate, the solvent was evaporated, and the residue was distilled under vacuum. The yield of pentafluorophenoxyacetone was 6.5 g (80%); bp 57° (at 1 mm); $n_D^{22} = 1.4385$. Found: C 44.90; 45.08; H 2.10; 2.21; F 39.45; 39.56%; mol. wt 228, 234 (isotherm. dist.) C₉H₅F₅O₂. Calculated: C 45.00, H 2.08; F 39.58%; mol. wt. 240. IR spectrum (in CCl₄): 1525 (fluorinated aromatic ring), 1735 cm⁻¹ (C = O). NMR H¹ spectrum (in CCl₄) comprised two signals shifted by 2.16 and 4.78 ppm (3:2) from HMS towards the weak field.

2, 4-Dinitrophenylhydrazone was produced according to [24]; mp 129-130° (from a mixture of alcohol with benzene). Found: F 22.67; 22.86; N 13.21; 13.39%. $C_{15}H_9F_5O_5N_4$. Calculated: F 22.60; N 13.34.

<u>1-Keto-4-(heptafluoronaphthoxy-1')-heptafluoro-1, 4-dihydronaphthalene (XIII)</u>. A crude product, obtained by oxidation of 7.2 g of heptafluoro- α -naphthol with 20 g of lead peroxide according to [3], was passed through a column containing 200 g of acidic Al₂O₃, in the benzene-hexane system (1:1). The yield of (XIII) was 2.8 g (39%); mp 96-98° (from hexane). The IR spectrum of the product was identical with the specimen obtained by reaction of quinnitrol (XII) with (IV).

<u>Thermolysis of Polyhalogenated Quinnitrols in the Absence of Oxygen.</u> Twenty-five grams of (I), freed from oxygen by multiple evacuation to 10^{-3} mm and helium blowing, was decomposed in a stream of helium at 60°; 19 g (97%) of a mixture of tetrafluorobenzoquinones was obtained, which was identical (by IR spectrum) with that produced under normal conditions [3]. The substance, which was condensed in a trap at -90°, boiled at -60 to -58° (according to [25], the boiling temperature of NOF is -61°). The IR spectrum of the gas was close to that of pure NOF [26].

By analogous decomposition of 20 g of quinnitrol (XIV) (prepared according to [4] at 140° were obtained 16.5 g (95%) of hexachloronaphthoquinone-1, 4 (mp 222°), whose IR spectrum was identical with that of a known specimen [4], and also 2.2 g of NOCl (mp -65 to -60°; bp -6 to -4°; according to [27]; mp -61° bp -6°). The IR spectrum of the gas was close to the spectrum of pure NOCl [28].

CONCLUSIONS

1. Polyfluorinated 4-nitrocyclohexadiene-2, 5-one-1 (quinnitrol) undergoes in neutral media a homolytic disruption of the C-N bond with formation of a polyfluoroaroxy radical and nitrogen dioxide.

2. Polyfluorinated phenoxy radicals are added to dienes-1, 3 in the 1- and 2-positions.

3. In the absence of substances catching the radicals, a recombination of the decomposition products of quinnitrol, during which NO_2 reacts via an oxygen atom, leads to the formation of polyfluorinated quinones.

LITERATURE CITED

- 1. G. G. Yakobson, V. D. Shteingarts, and N. N. Vorozhtsov, Jr., Zh. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva, 9, 701 (1964).
- 2. G. G. Yakobson, V. D. Shteingarts, and N. N. Vorozhtsov, Jr., Zh. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva, 9, 702 (1964).
- 3. V. D. Shteingarts, A. G. Budnik, G. G. Yakobson, and N. N. Vorozhtsov, Jr., Zh. Obshch. Khim., 37, 1537 (1967).
- 4. V. D. Shteingarts, O. I. Osina, G. G. Yakobson, and N. N. Vorozhtsov, Jr., Zh. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva, 11, 115 (1966).
- 5. V. D. Shteingarts, G. G. Yakobson, and N. N. Vorozhtsov, Jr., Dokl. Akad. Nauk SSSR, <u>170</u>, 1347 (1966).
- 6. C. Cook and R. Woodworth, J. Am. Chem. Soc., 75, 6242 (1953).
- 7. K. Ley and E. Müller Chem. Ber., 89, 1402 (1956).
- T. Zincke and W. Klostermann, Ber., 40, 681 (1907); K. Fries, Liebigs. Ann. Chem. 389, 315 (1912);
 K. Fries, W. Pense, and O. Peeters, Chem. Ber. 61, 1395 (1928); F. Bell, J. Chem. Soc., 1961, 5293.
- R. Ried, J. Am. Chem. Soc., 80, 219 (1958); E. Muller, A. Riecker, R. Mayer, and K. Scheffler, Liebigs Ann. Chem., <u>645</u>, 36 (1961); K. Dimroth and A. Berndt, Angew. Chem., 76, 434 (1964).
- 10. C. Bunton, E. Hughes, C. Ingold, D. Jacobs, M. Jones, G. Minkoft, and R. Ried, J. Chem. Soc., 1950, 2628.
- J. Conant and B. Chow, J. Am. Chem. Soc., 55, 3475 (1933); W. Hatchard, R. Lipscomb, and F. Stacey, J. Am. Chem. Soc., 80, 3636 (1958); R. Pummerer, G. Schmidutz, and H. Seifert, Chem., Ber., 85, 535 (1952).
- 12. F. Counturier, Liebigs Ann. Chem., 26, 493 (1892).
- 13. I. K. Korobeinicheva, A. K. Petrov, and V. A. Koptyug, Atlas of Spectra of Aromatic and Heterocyclic Compounds [in Russian], Nauka, Novosibirsk (1967).
- 14. J. Birchall and R. Haszeldine, J. Chem., Soc., 1959, 13.
- 15. J. Lawrenson, J. Chem., Soc., 1965, 1117.
- 16. A. Waring, Advances in Alicyclic Chemistry, Vol. 1, H. Hart and G. Karabatsos (editors), Academic Press, New York-London (1966), p. 129.

- 17. J. Feeney, L. Sutcliffe and S. Walker, Trans. Faraday Soc., 11, 2969 (1966).
- 18. K. Wallenfels and W. Draber, Angew. Chem., 70, 313 (1958).
- T. Zincke, W. Schneider, and W. Emmerich, Liebigs Ann. Chem., <u>328</u>, 268 (1903); T. Zincke and M. Buff, Liebigs Ann. Chem., 341, 318 (1905).
- 20. P. Gray, Trans. Faraday Soc., 51, 1367 (1955).
- R. Willstatter and V. Hottenroth, Ber., 37, 1775 (1904); W. Wislicenus and M. Waldmuller, Ber. 41 3334, 4169 (1908); W. Wislicenus and H. Gos, Ber, 44, 3491 (1911), E. Ziegler and T. Kappe, Monatsh., 95, 415 (1964).
- 22. A. A. Ivanov, Zh. Obshch. Khim., 16, 647 (1946).
- 23. L. Wall, W. Pummer, J. Fearn, and J. Antonucci, J. Res. Nat. Bur. Standards, 67A, 481 (1963).
- 24. J. Houben and T. Weyl, Methods of Organic Chemistry [Russian translation], Goskhimizdat (1965), p. 442.
- 25. A. Barg, Fluorine and Its Compounds' [Russian translation] Vol. 1, Symons (editor), Inostr. Lit. (1956), p. 80.
- 26. P. Woltz, G. Jones, and A. Nielsen, J. Chem. Phys., 20, 379 (1952).
- 27. F. M. Rapoport and P. P. Il'inskaya, Laboratory Methods of the Production of Pure Gases [in Russian], Goskhimizdat (1963), p. 202.
- 28. R. Pierson, A. Fletcher, and O. Ganz, Analyt. Chem., 28, 1218 (1956).