Journal of Organometallic Chemistry, 265 (1984) 27–34
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

GENERATION AND STABILIZATION OF FREE SELENIUM-CONTAINING RADICALS BY COMPLEX FORMATION

I.V. OLIFIRENKO, I.P. ROMM, E.N. GURYANOVA, V.V. TROITSKY, L.M. KATAEVA, V.A. CHERNOPLEKOVA and E.G. KATAEV

L. Ya. Karpov Physico-Chemical Research Institute, Moscow, 107120 (U.S.S.R.)

(Received October 18th, 1983)

Summary

The reactions of complex formation of some p-XC_6H_4Se–SeC_6H_4-p-X–MX_3-benzene (or cyclohexane) systems, where X = H, CH_3, F, Cl, Br and $MX_3 = GaCl_3$, $AlBr_3$, have been studied by calorimetry, cryoscopy, dielectric measurements, GLC, and ESR spectroscopy. Diaryldiselenides react with gallium trichloride in solution forming 1 : 1 complexes. The enthalpies of formation and the dipole moments of the complexes have been determined. Formation of diaryldiselenides complexes with aluminium bromide, which is a stronger acceptor, involves cleavage of the Se–Se and C–Se bonds in the diselenide molecule and yields stable selenium-centred radical complexes of the type $ArSeSe^{\cdot} \cdot AlBr_3$ (g-value 2.073) and $ArSe^{\cdot} \cdot AlBr_3$ (g value 2.033). In addition, the ESR spectrum reveals a singlet (g value 2.0025) assigned to a hydrocarbon radical. Corresponding di- and mono-selenides as well as biphenyls have been identified by GLC in the products of interaction of free radicals displaced from the mixture of radical complexes by an electron donor (diethyl ether, water) stronger than the radical.

Introduction

In modern chemistry the role of free radicals is widely recognized. It is known that numerous reactions involving organic disulphides follow a free-radical mechanism [1–3]. Some of the processes have found wide industrial application. The radicals of the $ArS^{\cdot}$ type are quite reactive, the lifetime of a $C_6H_5S^{\cdot}$ radical being, for example, 11 min at 171 K [4]. The radicals containing an unpaired electron on heavier atoms of Group VI elements (Se, Te) are poorly studied. Quite recently, evidence has been obtained that radicals of the $ArSe^{\cdot}$ and $ArSeSe^{\cdot}$ type exist at low temperatures [5,6].

Free radical stability can be increased by enhancing the degree of delocalization of electron spin density and by the steric shielding of the atoms carrying the unpaired electron [1–3]. Complex formation is a new efficient method of stabilizing

0022-328X/84/$03.00

free radicals containing a heteroatom [7,8]. The method was successfully used for preparing for the first time stable sulphur-containing radicals of the $ArS^{\cdot}MX_3$ type, where MX_3 is aluminium or gallium halide.

This paper reports the study of complex formation of aromatic diselenides p-$XC_6H_4Se{-}SeC_6H_4X$-p (where X = H, CH_3, F, Cl, Br) with strong electron acceptors (aluminium bromide and gallium trichloride) by cryoscopy, calorimetry, dielectric measurements, ESR spectroscopy and gas liquid chromatography.

Results and discussion

Diaryldiselenides react with gallium trichloride in benzene with the formation of $Ar_2Se_2 \cdot GaCl_3$ molecular complexes. This has been proved by the results of cryoscopic, calorimetric and dielectrometric titration of a gallium trichloride solution in benzene with the diselenides (direct titration) and of the diselenide solutions with gallium trichloride (back titration). The results of the direct and back titration were in accord. Figure 1 illustrates a Δt vs. m_2/m_1 curve (1) for cryoscopic titration of gallium trichloride solution in benzene (~ 0.05 mol/l) with diphenyl diselenide (Δt is the freezing point depression; m_1 and m_2 are the numbers of moles of the first ($GaCl_3$) and the second (Ar_2Se_2) components of the solution, respectively. A distinct inflection of the curve for $m_2/m_1 = 1$ indicates that a practically undissociated 1 : 1 complex is formed in the solution. At the point $m_2/m_1 = 1$, the molecular weight coincides to that calculated for $(C_6H_5)_2Se_2 \cdot GaCl_3$ complex. For $m_2/m_1 > 1$, the slope of the curve corresponds to the molecular weight of the diphenyl diselenide added. A slight increase in the depression within the first section ($m_2/m_1 < 1$) indicates that there is an equilibrium between the dimer and the monomer complex with benzene in a benzene solution of gallium trichloride [9], which shifts to the right hand side with the addition of diselenide:

$$\tfrac{1}{2}Ga_2Cl_6 + C_6H_6 \rightleftharpoons C_6H_6 \cdot GaCl_3 \qquad (1)$$

Figure 1 also presents a Q/m_1 vs. m_2/m_1 curve (2) for the calorimetric titration of a $(p\text{-}CH_3C_6H_4)_2Se_2$ solution with gallium trichloride (Q is the amount of heat liberated). The inflection for $m_2/m_1 = 1$ indicates that reaction 2 takes place:

$$D_{(sol)} + \tfrac{1}{2}Ga_2Cl_{6(sol)} = D \cdot GaCl_{3(sol)}, \quad -\Delta H_1 \qquad (2)$$

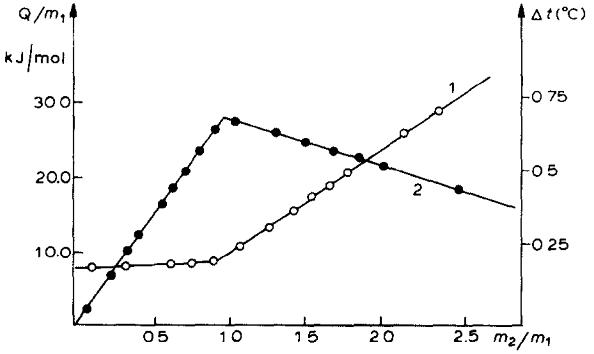

Fig. 1. Cryoscopic titration of a benzene solution of gallium trichloride with diphenyldiselenide (1) and calorimetric titration of a solution of di-*para*-tolyldiselenide with gallium trichloride (2).

TABLE 1

HEATS OF REACTION 2 ($-\Delta H_1$), ENTHALPIES OF FORMATION ($-\Delta H_c$) AND DIPOLE MOMENTS (μ_c) OF $Ar_2Se_2 \cdot GaCl_3$ (benzene, 298 K)

Diselenide	$-\Delta H_1$ (kJ/mol)	$-\Delta H_c$ (kJ/mol)	F_∞	R_D	μ_c (D)
$(p\text{-}CH_3C_6H_4)_2Se_2$	43.5	87.2	1660.5	119.4	8.6
$(C_6H_5)_2Se_2$	37.7	81.6	1259.8	109.9	7.5
$(p\text{-}BrC_6H_4)_2Se_2$	33.1	78.0	999.0	225.6	6.5
$(p\text{-}ClC_6H_4)_2Se_2$	35.6	79.5	905.3	119.9	6.2
$(p\text{-}FC_6H_4)_2Se_2$	36.0	79.9	–	–	–

The slope of the curve where $m_2/m_1 > 1$ corresponds to the heat of solution of gallium trichloride in benzene ($\Delta H = 9.2$ kJ/mol $GaCl_3$) [10].

The enthalpy of $C_6H_6 \cdot GaCl_3$ formation (reaction 1) is close to the energy of dimerization of gallium trichloride (43.8 kJ/mol $GaCl_3$) [10]. Consequently, the enthalpy of formation of $D \cdot GaCl_3$ ($-\Delta H_c$, reaction 3) can be derived from $-\Delta H_1$ by applying a correction for the energy of dimerization of gallium trichloride:

$$D_{(sol)} + GaCl_{3(sol)} = D \cdot GaCl_{3(sol)}, \; -\Delta H_c \qquad (3)$$

The values of ΔH_1 and ΔH_c are given in Table 1. Table 1 also lists the dipole moments of the complexes (μ_c, D) obtained by dielectrometric titration as well as the values of polarization obtained by Hedestrand extrapolation to indefinite dilution (P_∞) and molar refractions (R_D) calculated by the additive rule.

The complexes of diaryldiselenides with gallium trichloride are stable, highly polar molecular compounds in which a donor-acceptor bond is formed due to a vacant orbital of the gallium atom and an unshared electron pair (UEP) of a selenium atom of the diselenide bridge. Diaryldiselenides act as monodentate electron donors in complex formation with gallium trichloride. As is seen from Table 1, the stability of the complexes depends on the nature of the *para* substituents: electron donor substituents (CH_3, $\sigma_{para} = -0.17$) increase the enthalpy of complex formation whereas electron acceptor ones (F, Cl, Br, $\sigma_{para} = 0.062$, 0.227, 0.232, respectively) reduce it.

Fresh benzene solutions of complexes of diaryldiselenides with gallium trichloride produce no signals in ESR spectra. After 24 hours a brightly coloured oil is formed in the solutions with excess gallium trichloride and the signals of paramagnetic fragments appear in the ESR spectrum. Interaction of diaryldiselenides with stronger electron acceptors (aluminium bromide) in benzene or cyclohexane is accompanied by precipitation of paramagnetic products, even at early stages of the reaction. The reaction rate is maximum in the system diphenyl diselenide-aluminium bromide-benzene (or cyclohexane).

Figure 2 depicts the curves of cryoscopic titration of some diaryldiselenides dissolved in benzene with aluminium bromide. The fact that in the system with $(p\text{-}XC_6H_4)_2Se_2$, where X = Cl (curve 2) or X = Br (curve 3), the freezing point depression is constant up to the ratio $m_2/m_1 = 1$ indicates that 1 : 1 complexes are formed. This is also proved by the values of molecular weights at points $m_2/m_1 = 1$ which correspond, within the experimental error, to the $(p\text{-}XC_6H_4)_2Se_2AlBr_3$ complexes (X = Cl, $M_{exp} = 579$, $M_{calc} = 647$; X = Br, $M_{exp} = 694$, $M_{calc} = 737$). Thus,

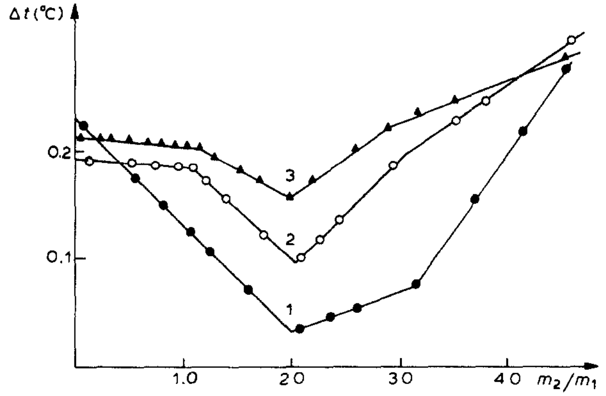

Fig. 2. Cryoscopic titration of $(p\text{-}XC_6H_4)_2Se_2$ in benzene with aluminium bromide, where X = H (1), X = Cl (2), X = Br (3).

by analogy with diaryldiselenide-gallium trichloride systems, aluminium bromide is bonded by diselenide molecules into a 1 : 1 donor-acceptor complex in the first stage of the reaction. A further addition of $AlBr_3$ up to $m_2/m_1 = 2$ causes an oily paramagnetic layer to form, and as a result the freezing point depression of the solution decreases.

In the $(C_6H_5Se)_2$-$AlBr_3$-benzene system, an oily, paramagnetic dark red product is formed at once; Δt correspondingly decreases so that when $m_2/m_1 = 2$ the freezing point of the solution is close to that of benzene. The slope of the final section of curve 1 (Fig. 2), where $m_2/m_1 > 3$, corresponds to the molecular weight of Al_2Br_6 in benzene ($M_{exp} = 530$, $M_{calc} = 533$). The linear sections of the cryoscopic titration curves over the region $2 < m_2/m_1 < 3$ are apparently related to the addition of extra $AlBr_3$ molecules to the complex.

Since the products of the reactions of diaryldiselenides with aluminium bromide are poorly soluble in benzene, neither calorimetric nor dielectric measurements were conducted. ESR spectroscopy was the main research tool in this case. The ESR spectra of the Ar_2Se_2-$AlBr_3$-C_6H_6 systems are characterized by three singlets (I, II, III). Figure 3 shows as an example the spectrum of the $(C_6H_5Se)_2$-$AlBr_3$-C_6H_6 system. Table 2 lists g values and widths (ΔH_{pp}) of the lines of the ESR spectra. The

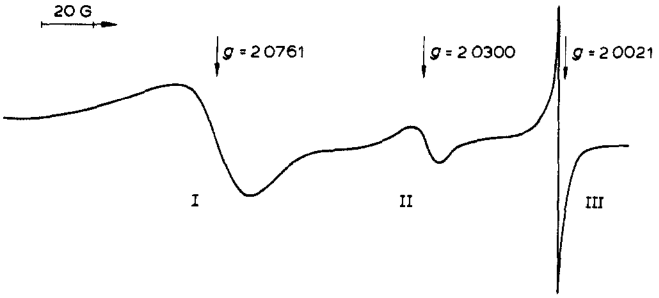

Fig. 3. ESR spectrum of $(C_6H_5)_2Se_2$-$AlBr_3$-C_6H_6 system.

TABLE 2

g VALUES AND LINE WIDTHS (ΔH_{pp}) OF ESR SPECTRA OF DIARYLDISELENIDE-ALUMINIUM BROMIDE-BENZENE SYSTEMS (298 K)

Diselenide	Numbers of signals in ESR spectrum		
	I	II	III
$(C_6H_5)_2Se_2$	2.0761 (23.75)	2.0300 (9.60)	2.0021 (1.67)
$(p\text{-}FC_6H_4)_2Se_2$	2.0694 (17.50)	2.0332 (5.83)	2.0025 (6.25)
$(p\text{-}ClC_6H_4)_2Se_2$	2.0730 (23.30)	2.0380 (11.70)	2.0027 (5.42)
$(p\text{-}BrC_6H_4)_2Se_2$	2.0744 (24.17)	2.0319 (12.50)	2.0026 (4.58)

high g values for singlets I (~ 2.070) and II (~ 2.030), differing greatly from the g value of a free electron (2.0023), and the significant line widths provide a good reason to assign the singlets to radicals containing a heavy atom (selenium in this case).

The research into the photodecomposition of some diaryldiselenides [4,6] has lead to the conclusion that not only the Se–Se bond but also the Se–C one can be cleaved with the result that selenium-centred radicals of the $ArSeSe^{\bullet}$ and $ArSe^{\bullet}$ type can be formed. This is the main difference between the photochemistry of diaryldiselenides and that of diaryldisulphides. In the latter case the cleavage of the S–S bond only is observed, leading to the formation of ArS radicals. The above difference may be observed during the reactions with strong electron-acceptors: formation and stabilization of $ArS^{\bullet}\cdot MX_3$ radical complexes in the case of diaryldisulphides [7,8] as well as formation and stabilization of selenium-centred $ArSe^{\bullet}\cdot MX_3$ and $ArSeSe^{\bullet}\cdot MX_3$ radical complexes in the case of diaryl diselenides.

On the basis of the above, singlet I ($g \sim 2.07$) can be assigned to a radical complex of the $ArSeSe^{\bullet}\cdot AlBr_3$ type and singlet II ($g \sim 2.03$) to radical complexes of the $ArSe^{\bullet}\cdot AlBr_3$ type. The assignment of singlet I to the $ArSeSe^{\bullet}\cdot AlBr_3$ radical complex is substantiated by the fact [4] that the g value of $ArSeSe^{\bullet}$ radicals must be higher than that of $ArSe^{\bullet}$ radicals. To prove such an interpretation of singlets I and II, we have studied the ESR spectrum of the $(C_6H_5)_2Se$ (monoselenide)-$AlBr_3$-C_6H_6 system, in which cleavage of the Se–C bond is likely to occur and the formation of a selenium-centred $C_6H_5Se^{\bullet}\cdot AlBr_3$ radical complex is possible. A singlet with a g value of 2.034, which may be assigned to singlet II of the $C_6H_5Se^{\bullet}\cdot AlBr_3$ radical complex, has been observed in the ESR spectrum of the system.

The third singlet in the ESR spectrum of Ar_2Se_2-$AlBr_3$-C_6H_6 system differed from that of the selenium-centred radicals both in the g value and shape (Fig. 3). Since the g value is close to that of a free electron, this singlet is assigned to a hydrocarbon radical resulting from homolytic fission of the Se–C bond. A phenyl radical formed due homolytic fission of the Se–C bond in diphenyldiselenide has previously been trapped by reaction with nitrosodurene [6].

The suggested interpretation of the reaction between diaryldiselenides and aluminium bromide has been proved experimentally by GLC. A stronger donor D (diethyl ether, water) expels the radical from the complex formed in the $(C_6H_5)_2Se_2$-$AlBr_3$-C_6H_6 system and gives rise to a $D\cdot AlBr_3$ complex and the combination products of the radicals expelled: diphenyldiselenide, diphenylselenide and diphenyl. No other products (including C_6H_5SeH and C_6H_5Br) were detected by GLC.

It should be noted that the radical complexes formed in the Ar_2Se_2-aluminium bromide-benzene system are very stable; the ESR spectra of samples sealed in ampoules are unchanged for months. However, the relative singlet intensities in the ESR spectra may change with time at a rate influenced by the nature of the aryl group and by the ratio of the electron-donor and electron-acceptor components. By analogy with $ArS^{\cdot}\cdot MX_3$ [7], the high stability of the selenium-centred radical complexes can be attributed to two effects: (a) a decrease in electron density on the selenium atom when the donor–acceptor bond is formed due to the unshared electron pair (UEP) of the selenium atom and the vacant orbital of the metal atom; this results in a lowering of the level of the unpaired electron orbital; (b) a steric shielding of the selenium atom by the acceptor molecule (MX_3).

It is not excluded that addition of $AlBr_3$ to $ArSe^{\cdot}\cdot AlBr_3$ and $ArSeSe^{\cdot}\cdot AlBr_3$ radical complexes with $-Se \rightarrow \overset{\diagdown\diagup}{Al}-Br \cdots Al\lessdot$ bonds will take place, as in the case of $ArS^{\cdot}\cdot 2AlBr_3$ radical complexes, provided there is a surplus of the electron acceptor. A second acceptor molecule added to the radical complex enhances steric shielding of the unpaired electron localized on the selenium atom, thus promoting radical-complex stabilization.

Radical complexes may be formed not only in a solution of the diaryldiselenide-aluminium bromide system but also in a melt of the corresponding components. Diselenides heated with aluminium bromide to 360 K form dark red melts which retain their colour after cooling. The ESR spectrum of a $(C_6H_5)_2Se_2$-$AlBr_3$ system in the form of a solidified melt (Fig. 4) is of a more complex nature than that of the same system in solution (Fig. 3) due to anisotropy of the g value in the ESR spectra of solids. To interprete more completely the ESR spectrum of the $(C_6H_5)_2Se_2$-$AlBr_3$ system in the form of a solidified melt, we have plotted not only the first derivative of the adsorption spectrum (Fig. 4, curve a) but the initial curve as well (curve b) integrated from the first derivative on a computer. A superposition of the signals produced by two radicals is the main feature of the ESR spectrum. One of these displays an anisotropic g value with principal values $g_1 = 2.1228$, $g_2 = 2.0857$, $g_3 = 2.0030$. The mean value, $g_{mean} = 1/3(g_1 + g_2 + g_3) = 2.0705$, coincides with the g value of singlet I in the ESR spectrum of the same system in solution (Fig. 3). The second radical is characterized by a narrow singlet with a g value of 2.0030 which either coincides with, or is close to, the g_3 value of the first radical. The signal from

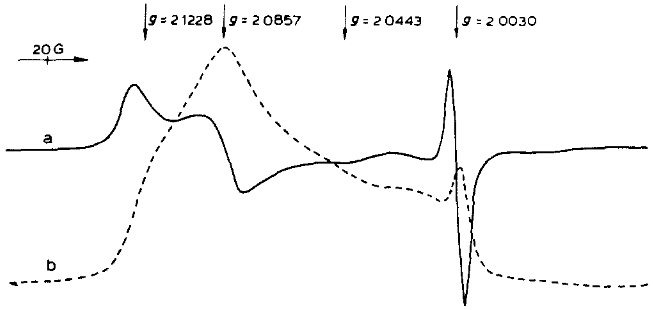

Fig. 4. ESR spectrum of $(C_6H_5)_2Se_2$-$AlBr_3$ system in the form of a solidified melt; (a) first derivative; (b) initial curve of ESR absorption spectrum (298 K).

radical II, with a g value of 2.0300 in the ESR spectrum of the $(C_6H_5)_2Se_2$-$AlBr_3$-C_6H_6 system in solution (Fig. 3), is masked in the spectrum of the solidified melt by a stronger signal from radical I, but is seen in the middle of the spectrum as inflections on the first curves of the ESR spectrum (g value 2.0443).

The narrow singlet in the ESR spectra of the diphenyldiselenide-aluminium bromide system as either a solution or a melt is a characteristic feature of the ESR spectra of this system. The g value approaches that of a free electron, indicating that the signal may be assigned to a hydrocarbon radical. Singlets of the same kind ($g \approx g_0$) have been observed in the ESR spectra of systems containing not only aluminium bromide and diphenyldiselenide but other diaryldiselenides as well (Table 2). All this points to a homolytic fission of not only the Se–Se bonds but also the Se–C ones in the diselenide molecules and to the formation of carbon-centred radicals in addition to the selenium-centred radical complexes of the $ArSe^{\bullet} \cdot AlBr_3$ and $ArSeSe^{\bullet} \cdot AlBr_3$ types. The singlet with a g value of 2.0025 observed in the ESR spectra of the Ar_2Se_2-$AlBr_3$-C_6H_6 systems (III, Table 2) may be due to the formation of either aryl radicals stabilized by complex formation with aluminium bromide or secondary hydrocarbon radicals, for example, a diphenyl cation radical. Unfortunately, most of the ESR spectra recorded of Ar_2Se_2-$AlBr_3$-C_6H_6 systems were of a singlet nature. In some instances a poorly resolved hyperfine structure due to a carbon-centred radical was observed.

In conclusion we note that the first stage of the reaction between diaryldiselenides and aluminium and gallium halides consists of the formation of D · A complexes at a very high rate. The second stage involving cleavage of the Se–Se and Se–C bonds on addition of a second halide molecule to the $Ar_2Se_2 \cdot MX_3$ complex and is somewhat slower; its rate depends on the nature of the acceptor and of the aryl fragment of the diselenide. The heats of formation and the dipole moments of the $Ar_2Se_2 \cdot GaCl_3$ complexes formed in the first stage could be measured due to the low rate of the second stage.

Experimental

All the diaryldiselenides were synthesized by procedures already described [12]. The compounds were purified and dried by repeated recrystallization until the actual and reported melting points coincided. The solvents and aluminium bromide were purified as reported [13]. Gallium trichloride was sublimed in vacuum.

The techniques of calorimetric and dielectrometric titration were as described [14]. The ESR spectra were recorded on a Bruker EP-420 spectrometer. The control samples of diselenides did not dissolve in benzene without an acceptor, nor did solutions of the halogenides of the metal in the absence of Ar_2Se_2 give ESR signals at room temperature. All the samples were prepared in an atmosphere of dry argon and degassed by repeated vacuum evacuation at 77 K.

All the experiments were carried out in an atmosphere of dry argon.

Acknowledgement

The authors wish to express their gratitude to Z.A. Sinitsyna for her kind assistance in conducting the experiments.

References

1 D. Nonhibel, J. Tedder and J. Walton, Radicals, Mir Publishers, Moscow, 1982, p. 265.

2 E.G. Rozantsev and V.D. Sholle, Organicheskaya khimiya svobodnykh radikalov (Free Radical Organic Chemistry), Khimiya, Moscow, 1979, p. 343.

3 V. Ingold and B. Roberts, Free Radical Substitution Reactions, Mir Publishers, Moscow, 1974, p. 255.

4 U. Schmidt, A. Muller and K. Markau, Chem. Ber., 97 (1964) 405.

5 J. Bergman, N. Eklund and T. Eriksen, J. Lind. Acta Chem. Scand., A32 (1978) 455.

6 R. Franzi and M. Geoffroy, J. Organomet. Chem., 218 (1981) 321.

7 E.N. Guryanova, I.P. Romm, L.A. Ganyushin, I.A. Abronin and V.A. Chernoplekova, Dokl. Akad. Nauk SSSR, 248 (1979) 108.

8 L.A. Ganuyshin, E.N. Guryanova, I.P. Romm and L.A. Lobanova, Zh. Org. Khim., 49 (1979) 2090.

9 I.P. Romm, E.N. Guryanova, E.N. Kharlamova, R.R. Shifrina, N.N. Shapetko and K.A. Kocheshkov, Dokl. Akad. Nauk SSSR, 189 (1969) 810.

10 I.P. Romm, E.N. Kharlamova and E.N. Guryanova, Zh. Org. Khim., 42 (1972) 2246.

11 A.A. Vyazgina, I.P. Romm, E.N. Guryanova, V.V. Troitsky and R.R. Shifrina, Zh. Org. Khim., 53 (1983) 1368.

12 L.A. Sorokina, Kand. diss., Kazan, 1975.

13 I.P. Romm and E.N. Guryanova, Zh. Org. Khim., 38 (1968) 1927.

14 E.N. Guryanova, I.P. Goldstein and I.P. Romm, Donorno-aktseptornaya svyaz (Donor-Acceptor Bonds), Khimiya, Moscow, 1973, p. 38.