ELECTROPHILIC HYDROGEN SUBSTITUTION REACTIONS IN η^5-INDENYL AND η^5-FLUORENYLTRICARBONYL COMPLEXES OF MANGANESE AND RHENIUM

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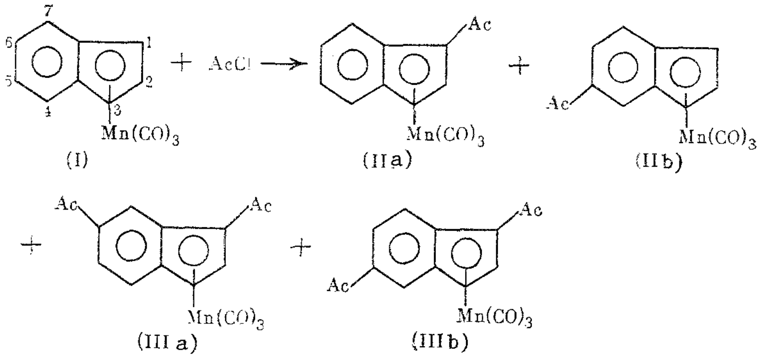
Hydrogen substitution reactions in the π-ligands of neutral η^5-indenyl and η^5-fluorenyl transition metal complexes have not been studied much previously. Some preliminary results concerning the acylation of η^5-indenyltricarbonyl Mn and Re complexes have been reported in the literature [1]. It was found that the reaction of η^5-$C_9H_7Mn(CO)_3$ (I) with AcCl in the presence of $AlCl_3$ leads to the formation of isomeric monoacetyl derivatives (IIa, b), as well as diacetyl derivatives (IIIa, b).



PMR spectral analysis revealed that in (IIa) the acetyl group is located on the 5-membered ring, whereas in (IIb) it is located on the 6-membered ring of the η^5-indenyl ligand. The PMR spectra of the diacetyl complexes (IIIa) and (IIIb) are very similar in the region corresponding to signals of the 5-membered ring protons, and significantly different in the region corresponding to the aromatic proton signals. The spectrum of (IIIa) contains two singlets at δ 7.77 and 9.00 ppm, whereas the spectrum of (IIIb) contains a doublet of doublets (A portion, AB system), δ_A 7.93 ppm, a doublet (B portion, AB system), δ_B 8.38 ppm, and a multiplet centered at δ 8.55 ppm. It would seem reasonable, therefore, that in (IIIa) the CH_3CO group is located in the 6-position, and in (IIIb), in the 5-position of the η^5-indenyl ligand.

The yields and isomeric ratios of acetylation products are determined by the reaction conditions. For example, in the acetylation of (I) by the $AcCl \cdot AlCl_3$ complex in CH_2Cl_2, at a (I):AcCl:$AlCl_3$ ratio of 1:7:2, the total yield of monoacetylated products was 67% (63% (IIa) and 37% (IIb)). At a reagent ratio of 1:14:4, the yield of (IIa, b) changed very little, but the yield of diacetyl derivatives was increased from 4 to 14%. In contrast, in the acetylation of (I) in the presence of solid $AlCl_3$, substitution in the 6-membered ring predominated; the product mixture consisted of 60% (IIb) and 40% (IIa).

In order to compare the reactivities of η^5-indenyl and η^5-cyclopentadienyl ligands coordinated to $Mn(CO)_3$, we carried out the competitive acetylation reaction of (I) and $C_5H_5Mn(CO)_3$ (IV). The acetylation reaction was done using 1 equiv. AcCl to one equivalent of the complexes (I) and (IV) in the presence of 2 equiv. $AlCl_3$ in CH_2Cl_2 at 20°C. The ratio of reaction products was determined by PMR via integration of the CH_3CO group signals. It was found that the reactivity of the η^5-indenyl ligand was significantly higher than that of the η^5-cyclopentadienyl ligand. Unreacted (IV) (68%) was isolated from the reaction mixture, whereas (I) was not detected in the product mixture. The concentration of monoacetylated η^5-indenyltricarbonylmanganese derivatives in the reaction mixture was

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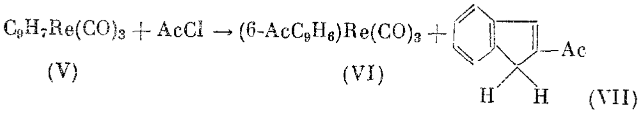
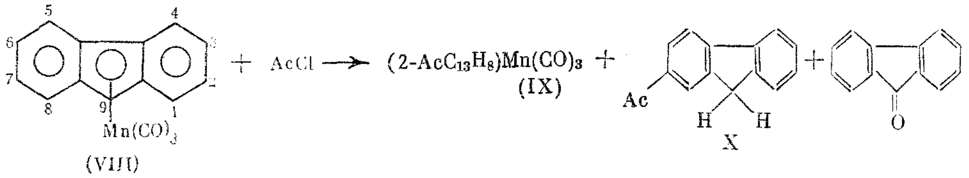
5-8 times greater than that of $AcC_5H_4Mn(CO)_3$. However, if one compares only the five-membered ring of the η^5-indenyl ligand in (I) with the η^5-cyclopentadienyl ligand in (IV), then the ratio becomes much smaller, namely, $(1\text{-}AcC_9H_6)Mn(CO)_3 : (AcC_5H_4)Mn(CO)_3 = 1.9\text{-}2.8$.

Acetylation of η^5-$C_9H_7Re(CO)_3$ (V) with AcCl in the presence of $AlCl_3$ led to the formation of the monoacetyl complex (VI) (5%) and 2-acetylindene (VII) (17.5%).



The formation of 2-acetylindene during the acetylation of (V) indicates that cleavage of the metal-π-ligand bond takes place, which does not occur in the case of the reactions of η^5-$C_5H_5Re(CO)_3$ [2] or (I). Mass spectroscopic analysis has shown that the strength of the metal-π-ligand bond is significantly greater in (V) than in (I) in the gas phase [3]. The difference in the behavior of the analogous Mn and Re complexes under acetylation conditions must then be associated with a difference in the mechanism of acetylation. It can be assumed that substitution of a hydrogen atom in the 5- or 6-membered ring of the η^5-indenyl ligand in (I) occurs via direct attack of an acylium cation. This mechanism is analogous to that postulated for the hydrogen exchange reaction of η^5-$C_5H_5Mn(CO)_3$ in the presence of acids [4], based on kinetic isotope effect data. In the case of (V), where the metal atom is much more basic [5], and the 5-membered ring coordinated to the metal atom exhibits lower electron density, due to the greater electron withdrawing effect of the $Re(CO)_3$ group [6], it is assumed that electrophilic attack occurs either directly on the 6-membered ring or at the metal atom. An intermediate characterized by a Re—electrophile bond has been shown to be quite stable [7]. Transfer of the electrophile from the Re atom to the 5-membered ring of the π-ligand is unfavorable, and instead the intermediate is stabilized via cleavage of the π-ligand and its subsequent acetylation.

Acylation of η^5-$C_{13}H_9Mn(CO)_3$ (VIII) with AcCl in the presence of $AlCl_3$ leads to the formation of $(2\text{-}AcC_{13}H_8)Mn(CO)_3$, 2-acetylfluorene, and fluorenone:



The structure of (IX) was solved based on elemental analysis and IR, mass, and PMR spectroscopy. The PMR spectrum of (IX) in $(CD_3)_2CO$ exhibits a singlet at δ 2.68 ppm, corresponding to the methyl group protons, a singlet at δ 9.16 ppm due to the protons in the 1-position, and a doublet of doublets at δ 7.63 and 7.86 ppm for the remaining protons of the substituted 6-membered ring. The protons of the unsubstituted 6-membered ring appear as a series of multiplets at δ 7.66, 7.35, and 8.41 ppm, whereas the proton of the 5-membered ring appears as a singlet at δ 6.01 ppm. Thus, acylation of (VIII) occurs regioselectively at the 2-position of the fluorenyl ligand, regardless of the reaction conditions, and is accompanied by cleavage of the manganese-π-ligand bond. The reduced strength of the Mn-π-ligand bond in η^5-$C_{13}H_9Mn(CO)_3$ compared to η^5-$C_9H_7Mn(CO)_3$, as indicated by the acetylation results, is consistent with the results determined in the gas phase [8].

The hydrogen isotope exchange (HIE) reaction of (I) in acidic media was studied and revealed that (I) is practically inert to the HIE reaction in a mixture of CH_3COOD and D_2SO_4 in CH_2Cl_2. In more acidic solution, in a mixture of $CF_3COOD/D_2SO_4/CH_2Cl_2$, (I) does undergo exchange of hydrogen atoms of the π-ligand with deuterium, although other reactions also take place simultaneously: alkylation, acylation, and metallotropic rearrangement. In order to clarify these processes, we investigated the reaction of (I) with a mixture of undeuterated acids under the same conditions. The following were isolated from this reaction: (I) (25%), and complexes (XI) and (XII), in up to 20% yield. IR spectroscopic analysis also identified the presence of a CF_3CO-substituted η^5-indenylmanganesetricarbonyl derivative and the product corresponding to $\eta^5 \to \eta^6$-metallotropic rearrangement of (I) in the form of the salt (XIII). It is assumed that complexes (XI) and (XII) are formed as a result of alkylation of (I) by protonated indene in acidic solution, which appears as a consequence of cleavage of the metal-π-ligand bond. When the HIE reaction of (I) was carried out in a mixture of $CF_3COOD/D_2SO_4/CH_2Cl_2$, deuterium-containing analogs of complexes (XI) and (XII) were isolated, in addition to deuterated (I). Using PMR spectroscopy it was established that under hydrogen isotope exchange reactions in the presence of acids, hydrogen atoms on both the 5-membered as well as 6-membered rings of the π-ligand in η^5-$C_9H_7Mn(CO)_3$ participate, although substitution at the 5-membered ring predominates under the conditions of this experiment.

EXPERIMENTAL

All operations were carried out in an inert atmosphere. η^5-$C_9H_7Mn(CO)_3$ and η_5-$C_9H_7Re(CO)_3$ were synthesized according to [8], η^5-$C_{13}H_9Mn(CO)_3$ according to [9]. IR spectra were obtained on a UR-20 and Specord 71-IR spectrophotometers, while PMR spectra were recorded on a Bruker WP-200SY (200 MHz) spectrometer relative to HMDS. Mass spectra were obtained on an MS-30 instrument at 70 eV.

Competitive Acylation of (I) and (IV). A solution of 0.5 g (1.97 mmole) (I) and 0.41 g (1.97 mmole) (IV) in 10 ml CH_2Cl_2 was treated with 0.53 g (3.97 mmole) $AlCl_3$ and 0.16 ml (2.03 mmole) AcCl with stirring. After 1 h at 20°C the mixture was poured onto ice water, and the organic layer was separated, washed with water, dried, and evaporated. The residue was subjected to column chromatography on SiO_2; elution with petroleum ether gave a yellow band, which yielded 0.28 g (68.1%) of (IV), and elution with chloroform gave an orange band, which yielded 0.47 g of a mixture of acetylated derivatives of complexes (I) and (IV). The following ratios were calculated for this mixture by PMR: $AcC_9H_6Mn(CO)_3:AcC_5H_4Mn(CO)_3$ = 4.8:1; $(1\text{-}AcC_9H_6)Mn(CO)_3:AcC_5H_4Mn(CO)_3$ = 1.85:1; $(5\text{-}AcC_9H_6)Mn(CO)_3:(1\text{-}AcC_9H_6)Mn(CO)_3$ = 1.6:1; yields of the isomers were also determined in this way, $(AcC_9H_6)Mn(CO)_3$ = 69%, and $AcC_5H_4Mn(CO)_3$ = 9.8%. When the experiment was repeated, $AcC_9H_6Mn(CO)_3:AcC_5H_4Mn(CO)_3$ ratios of 7.6:1 and 2.8:1 were found.

Acetylation of (V). A solution of 0.73 g (1.90 mmole) (V) in 50 ml CH_2Cl_2 was treated with stirring with 0.49 g (3.68 mmole) $AlCl_3$ and 0.21 ml (2.6 mmole) AcCl. After 2.5 h at 20°C the reaction mixture was poured onto water, and the organic layer was separated, washed, dried, and evaporated. The residue was subjected to column chromatography on Fluorisil. The first zone was eluted with petroleum ether—ether (2:1), the second with ether. After repeat chromatography, 0.05 g (17.5%) of (VII) (petroleum ether—ether, 2:1 eluent was isolated, mp 46-48°C (from pentane). IR spectrum (ν, cm^{-1}, CH_2Cl_2) 1669 s (C=O). Mass spectrum (m/z): M^+ 158, $[M-CH_3]^+$ 143, $[M-C_2H_2O]^+$ 116, $[M-CH_3CO]^+$ 115. Found: C 83.36; H 6.56%. $C_{11}H_{10}O$. Calcd.: C 83.52; H 6.37%. PMR spectrum (δ, ppm, $(CD_3)_2CO$): 3.58 d (2H, J = 1.8 Hz, H^3, $H^{3'}$), 7.32 m (2H, H^5, H^6), 7.51 m (1H, J = 0.9 Hz, H^4), 7.75 m (1H, J = 1.9, J = 0.6 Hz, H^1), 7.58 m (1H, H^7), 2.40 s (3H, CH_3). Repeat chromatography of the second zone yielded 0.04 g (5%) of (VI) (ether eluent), mp 108-110°C. IR spectrum (ν, cm^{-1}, CH_2Cl_2): 1932, 2024 (C≡O), 1682 (C=O). Mass spectrum (m/z): ^{187}Re M^+ 428, $[M-CO]^+$ 400, $[M-2CO]^+$ 372, $[M-3CO]^+$ 344, $[M-3CO-H_2]^+$ 342, $[M-4CO]^+$ 316, $[M-4CO-H_2]^+$ 314.

Acylation of (VIII). A solution of 0.3 g (0.99 mmole) (VIII) in 30 ml CH_2Cl_2 was stirred at 20°C and 0.26 g (1.95 mmole) $AlCl_3$ and 0.23 ml (2.92 mmole) AcCl were added. After 1 h the mixture was poured onto water, and the organic layer was separated, washed with water, dried, and evaporated. The residue was subjected to column chromatography on Fluorisil; elution with CH_2Cl_2 gave an orange band, which after repeat chromatography gave 0.1 g (29%) of (IX) (petroleum ether—ether, 1:1 eluent), mp 120-121°C (from pentane—CH_2Cl_2); mass spectrum (m/z): M^+ 346, $[M-CO]^+$ 318, $[M-2CO]^+$ 290, $[M-3CO]^+$ 262, $[M-3CO-Mn]^+$ 207, $[M-3CO-Mn-COCH_3]^+$ 164; Mn^+55. IR spectrum (ν, cm^{-1}, CH_2Cl_2): 2030, 1952 (C≡O), 1687 (C≡O). PMR spectrum (δ, ppm, $(CD_3)_2CO$): 2.68 s (3H, CH_3), 9.16 s (1H, H^1), 7.86 d (1H, J = 1.2 Hz, H^3), 7.63 d (1H, H^4), 7.66 m (1H, H^5), 7.35 m (2H, H^6, H^7), 8.41 m (1H, H^8), 6.01 s (1H, H^9). Found: C 62.83; H 3.49; Mn 15.17%. $C_{18}H_{11}MnO_4$. Calculated: C 62.44; H 3.20; Mn 15.87%. A mixture of organic products was also isolated (petroleum ether eluent), which after two-fold chromatography gave 0.02 g (10%) (X), mp 122-124°C, mass spectrum (m/z): M^+ 208, $[M-CH_3]^+$ 193, $[M-CH_3CO]^+$ 165. IR spectrum (ν, cm^{-1}, CH_2Cl_2): 1686 s, 1616 w, 1575 w. PMR spectrum (δ, ppm, $(CD_3)_2CO$): 2.58 s (3H, CH_3), 3.94 s (2H, H^9), 8.14 s (1H, H^1), 8.00 d (1H, J = 9.5 Hz, H^3), 7.94 d (2H, J = 8.9 Hz, H^4, H^5), 7.61 d (1H, H^8), 7.37 m (2H, H^6, H^7).

Hydrogen Isotope Exchange Reaction of (I) in a Mixture of $CH_3COOD/D_2SO_4/CH_2Cl_2$. A solution of 0.36 g (1.4 mmole) (I) in 3.9 ml (61.0 mmole) CH_2Cl_2, 2.4 ml (41.3 mmole) CH_3COOD (80% D), and 0.09 ml (1.6 mmole) D_2SO_4 (80% D) was maintained at 20°C for 20 days;

the mixture was poured onto water, CH_2Cl_2 was added, and the organic layer was separated, washed with water to a neutral point, and dried over $CaCl_2$. The solvent was evaporated under vacuum, and the residue was chromatographed on a SiO_2 column, 100/160 μ. Elution with petroleum ether gave 0.36 g (100%) of (I). The concentration of deuterium in the sample, as determined by mass spectroscopy, was 0.5 atom %.

Reaction of (I) with a Mixture of $CF_3COOH/H_2SO_4/CH_2Cl_2$. A solution of 0.36 g (1.4 mmole) (I) in 3.9 ml (61.0 mmole) CH_2Cl_2, 2.4 ml (32 mmole) CF_3COOH, and 0.09 ml H_2SO_4 (reagent grade) was maintained at 20°C for 47 h; the mixture was poured onto water, CH_2Cl_2 was added, and the organic layer was separated, washed with water to a neutral point, and dried. Solvent was removed in vacuo, and the residue was chromatographed on a SiO_2 column. Two yellow fractions were eluted with light petroleum ether, and fraction (III) was eluted with petroleum ether—$CHCl_3$ (10:1). After solvent evaporation from the first fraction, 0.09 g (25%) (I) was obtained. Fraction II gave (XI), 0.05 g (19%), ν(C≡O) (CH_2Cl_2) 2018, 1940 cm^{-1}. Found: C 68.76; H 4.71; Mn 14.84%. $C_{21}H_{15}MnO_3$. Calculated: C 68.11; H 4.05; Mn 14.86%. PMR spectrum (δ, ppm, $(CD_3)_2CO$)*: 5.20 d (1H, H^1) 5.36 d (1H, H^2), 7.82 m (1H, H^3), 7.20 m and 7.28 m (2H, H^4, H^5), 7.57 m (1H, H^6), 4.74 t (1H, H^7), 3.01 and 3.09 (AB-system 2H, H^8, $H^{8'}$), 2.20 and 2.66 (2H, H^9, $H^{9'}$), 6.82 d (1H, H^{10}), 7.02 t (1H, H^{11}), 7.13 t (1H, H^{12}), 7.25 m (1H, H^{13}), J (Hz)†: $H^1H^2 = 3$, $H^7H^{8'} = 0$, $H^7H^8 = 8$, $H^8H^8 = 15$, $H^9,H^{9'} = 13$, $H^7H^{9'} = 0$, $H^7H^9 = H^8H^9 = H^{8'}H^9 = 9$, $H^8H^{9'} = 7$. Mass spectrum (m/z): M^+ 370 $[M-2CO]^+$ 314, $[M-3CO]^+$ 286, $[M-3CO-Mn]^+$ 231, $[M-3CO-Mn-2H]^+$ 229, $C_9H_9^+$ 117, $C_9H_8^+$ 116, $C_9H_7^+$ 115, Mn^+ 55. Fraction III (0.05 g) was chromatographed once more on Silufol plates. Elution with a mixture of ether—hexane (1:7) gave (XII), ν(C≡O) (CH_2Cl_2): 2013, 1932 cm^{-1}. PMR spectrum (δ, ppm, $(CD_3)_2CO$): 5.26 s (1H, H^1), 7.87 m (2H, H^2, H^5), 7.34 m (2H, H^3, H^4), 4.72 t (2H, H^6, H^{13}), 3.00 m (4H, H^7, $H^{7'}$, H^{14}, $H^{14'}$), 2.19 and 2.62 (4H, H^8, $H^{8'}$, H^{15}, $H^{15'}$), 6.77 d (2H, H^9, H^{16}), 6.96 t (2H, H^{10}, H^{17}), 7.06 t (2H, H^{11}, H^{18}), 7.18 d (2H, H^{12}, H^{19}), J (Hz): $H^8H^{8'} = 13$, $H^6H^7 = 8$, $H^8H^7 = H^8H^7 = H^{8'}H^{7'} = 9$, $H^{8'}H^7 = 9$.

Mass spectrum (m/z): M^+ 486 $[M-3CO]^+$ 402, $[M-3CO-Mn-2H]^+$ 345, $C_9H_9^+$ 117. A substance was also isolated at the same time, which according to its IR spectrum can be assigned the structure $(CF_3CO)_nC_9H_{7-n}Mn(CO)_3$, where n = 1 or 2. IR spectrum (CH_2Cl_2, ν, cm^{-1}): 1720 (C=O), 1942, 2020 (C≡O).

The water solution remaining after decomposition of the reaction mixture with water and removal of the organic layer was treated with 0.3 g (3 mmole) NH_4BF_4 and evaporated to dryness. The solid residue was extracted with acetone, and the solution was filtered and evaporated to dryness. The residue was washed with ether and extracted with chloroform. The IR spectrum of the extract contained bands at 2076 (ν(C≡O)) and 2013 cm^{-1}, corresponding to (XIII).

Hydrogen Isotope Exchange Reaction of (I) in a Mixture of $CF_3COOD/D_2SO_4/CH_2Cl_2$. A mixture of 0.36 g (1.4 mmole) (I) in 3.9 ml (61.0 mmole) CH_2Cl_2, 2.4 ml (32.0 mmole) CF_3COOD (80% D), and 0.09 ml (1.6 mmole) D_2SO_4 (80% D) was treated at 20°C for 44 h; the mixture was poured onto water and CH_2Cl_2 was added. The organic layer was separated, washed with water to a neutral point, and dried. The solvent was evaporated and the residue was subjected to column chromatography on SiO_2 (100-160μ). Elution with petroleum ether gave two yellow zones. Fraction I: d-$C_9H_7Mn(CO)_3$, 0.02 g (5.6%). The concentration of deuterium as determined by mass spectroscopy was 14 atom %; 74.5% of the molecules participated in the hydrogen exchange reaction.

The PMR spectrum revealed that hydrogens on the 5-membered ring participated two times as much in the HIE reaction as did the protons of the 6-membered ring. Fraction II: d-C_9H_9-$C_9H_6Mn(CO)_3$ (7.7%), mp 131-138°C (dec.). The concentration of deuterium in the sample from its mass spectrum was 17.5 atom %; 98% of the molecules underwent HIE. Fraction III: d-$(C_9H_9)_2C_9H_5Mn(CO)_3$, 0.03 g (13%).

CONCLUSIONS

1. Upon acetylation or isotopic hydrogen exchange in acidic media, hydrogen substitution in η^5-$C_9H_7Mn(CO)_3$ occurs at both the 5-membered and 6-membered rings of the η^5-indenyl ligand.

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*Hydrogen atoms located cis to H^7 are designated by H', and those located trans by H).
†J between the ortho protons of the phenyl ring is ca. 7 Hz.

2. Acetylation of η^5-$C_9H_7Re(CO)_3$ and η^5-$C_{13}H_9Mn(CO)_3$ occurs only at the six-membered ring of the π-ligand and is accompanied by cleavage of the metal—π-ligand bond.

3. Competitive acetylation revealed that the η^5-indenyl complex η^5-$C_9H_7Mn(CO)_3$ is more reactive than the η^5-cyclopentadienyl complex η^5-$C_5H_5Mn(CO)_3$ with respect to electrophilic hydrogen substitution reactions.

LITERATURE CITED

1. I. A. Lobanova, V. I. Zdanovich, and N. E. Kolobova, Izv. Akad. Nauk SSSR, Ser. Khim. 2606 (1982).
2. E. O. Fischer and W. Fellmann, J. Organometal. Chem., 1, 191 (1967).
3. V. F. Sizoi, V. A. Semenov, V. I. Zdanovich, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2153 (1985).
4. F. S. Yakushin, V. N. Setkina, N. V. Kislyakova, et al., ibid, 316 (1972).
5. B. V. Lokshin, Ph. D. Dissertation, Moscow (1977).
6. S. P. Gubin, A. A. Koridze, N. A. Ogorodnikova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1170 (1981).
7. A. G. Ginsberg, V. N. Setkina, and D. N. Kursanov, ibid, 1155 (1983).
8. V. I. Zdanovich, I. A. Lobanova, and N. E. Kolobova, ibid, 2149 (1984).
9. N. E. Kolobova, I. A. Lobanova, and V. I. Zdanovich, ibid, 1651 (1980).