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DZHEMILEV REACTION IN THE SYNTHESIS OF FIVE-MEMBERED SULFUR AND SELENIUM HETEROCYCLES*

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A one-pot methods were developed for the synthesis of five-membered sulfur and selenium heterocycles based on the consecutive cyclometallation of olefins, allenes, and acetylenes using alkyl and haloalkyl derivatives of Al and Mg in the presence of catalytic amounts of titanium and zirconium complexes to give the corresponding alumina- and magnesacarbocycles in situ, which, without further purification, were introduced into reaction with sulfur or selenium, leading to various tetrahydrothiophenes, thiophenes, tetrahydroselenophenes, and selenophenes.

Keywords: aluminacyclopentanes, magnesacyclopentanes, selenophenes, tetrahydroselenophenes, tetrahydrothiophenes, thiophenes, metal complex synthesis.

Thiophene is separated from the coking products of mineral coal or obtained by the thermal reaction of C_4-hydrocarbons with sulfur, hydrogen sulfide, and SO_2 [1-3]. One of the most popular synthetic methods for the preparation of tetrahydrothiophenes and selenophenes is a method based on use of the Yur'ev reaction [4, 5].

Along with these methods, the synthesis of five-membered heterocycles by means of replacing transition metal atoms, in particular, the zirconium atom in zirconacyclopentanes, zirconacyclopentenes, and zirconacyclopentadienes by sulfur and selenium atoms, has been found feasible [6-9]. Unfortunately, this method has not found common use due to the need to employ stoichiometric amounts of the zirconacycloalkanes and the difficulty in preparing these organometallic precursors.

The reactions of metallacycloalkanes, prepared *in situ* using nontransition metals, aluminacyclopentanes [10-12], magnesacyclopentanes [13, 14], and their derivatives prepared *in situ* by the Dzhemilev reaction by means of the catalytic cycloalumination and cyclomagnesation of unsaturated compounds using alkyl Mg and Al derivatives by the action of catalysts derived from Ti and Zr complexes, with S_8 and Se hold promise for the synthesis of five-membered heterocycles (Scheme 1).

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* Dedicated to Academician B. A. Trofimov of the Russian Academy of Sciences on the occasion of his seventieth jubilee.

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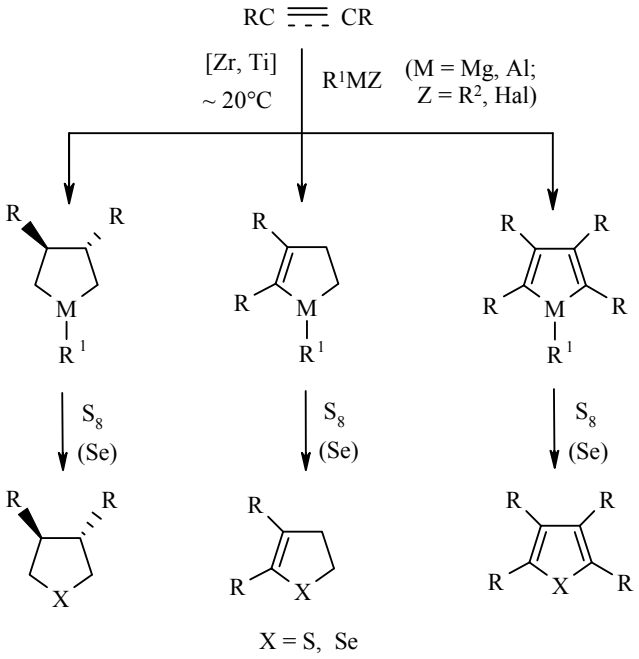
Scheme 1



The reactions shown in this scheme were studied by the present authors in the case of α-olefins [15-18], norbornene [19], linear allenes, and acetylenes [20-22].

In the present work, we have expanded the scope of catalytic cycloalumination and cyclomagnesation of unsaturated compounds in the synthesis of five-membered heterocycles. We also have attempted to clarify the feasibility of using cyclic 1,2-dienes, acetylenes, and methylenecycloalkanes in this reaction.

Methylenecyclobutanes, 1,2-cyclononadiene, and disubstituted acetylenes were selected as substrates for this study. We assumed that the catalytic cycloalumination and cyclomagnesation of these compounds using $AlEt_3$, $EtAlCl_2$, and RMgX would lead to new efficient methods for the synthesis of fused tetrahydrothiophenes, thiophenes, and tetrahydroselenophenes.

In previous work [23], we carried out the selective cycloalumination of methylenecyclobutane using $AlEt_3$ in the presence of 5 mole % Cp_2ZrCl_2 in pentane over 4 h to give 6-ethyl-6-aluminaspiro[3.4]octane, which, upon treatment with $SOCl_2$ *in situ* is converted to 6-thiaspiro[3.4]octane in 62% yield.

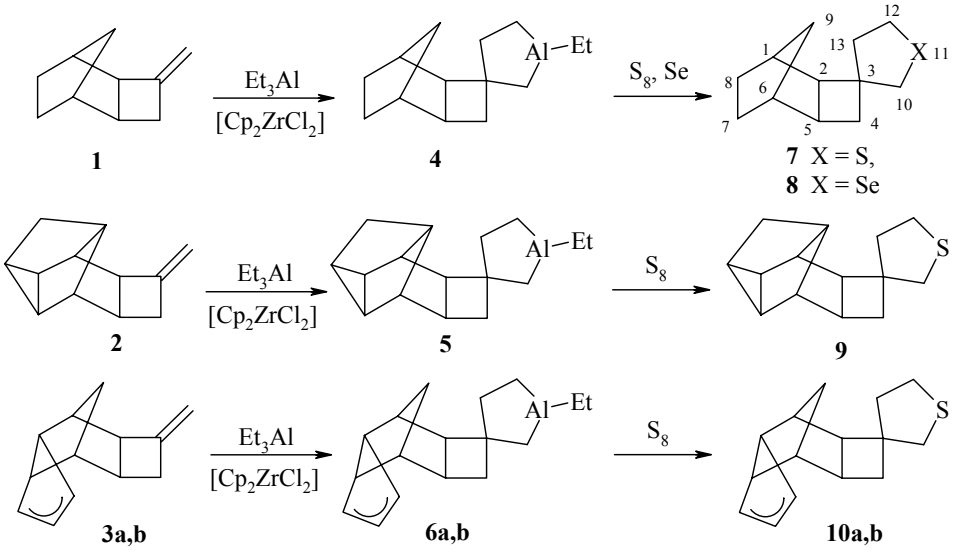
In a continuation of this study and in an attempt to synthesize spirothiophans, we were the first to investigate the catalytic cycloalumination of 3-methylene-*exo*-tricyclo[4.2.1.$0^{2,5}$]nonane (**1**), 3-methylene-*exo*-pentacyclo-[5.4.0.0^{2,5}.0^{6,10}.0^{9,11}]undecane (**2**), 9-methylene-*endo*- (**3a**), and 9-methylene-*exo*-tetracyclo[5.4.1.0^{2,6}.0^{8,11}]dodec-3(4)-ene (**3b**) under the conditions described to give the corresponding aluminaspiro[3.4]octanes, namely, spiro-[tricyclo[4.2.1.0^{2,5}]nonane-3,3'-(1'-ethylaluminacyclopentane)] (**4**), spiro[pentacyclo[5.4.0.0^{2,5}.0^{6,10}.0^{9,11}]undecane-3,3'-(1'-ethylaluminacyclopentane)] (**5**), and spiro[tetracyclo[5.4.0^{2,6}.0^{8,11}]dodec-3(4)-ene-9,3'-(1'-ethylalumina-cyclopentanes)] **6a,b**. These spiro products react readily *in situ* with S_8 and Se to give spirotetrahydro-thiophenes **7, 9,** and **10** and selenophene **8** (Scheme 2).

The structure of **8** was demonstrated by 1D (^{1}H, ^{13}C, Dept 135°) and 2D (HSQC, HMBC, HH, COSY, and NOESY) NMR spectroscopy.

Thus, the existence of a spiroselenophene ring was unequivocally indicated by two isolated proton spin systems: the geminal H-10 system at 2.62 and 2.86 ppm (^2J = 10 Hz) and strongly coupled vicinal AA'BB' system at C-12 and C-13. A characteristic indication of the presence of selenium is the finding of direct

coupling constants $^{1}J_{C\text{-}Se}$ = 48 Hz observed in the spectrum due to satellites for atoms C-12 and C-13 at the signals δ 20.3 and 29.0 ppm, respectively. The *exo* configuration of the cyclobutane fragment is indicated by the vicinal coupling constant $^{3}J_{H\text{-}2,5}$ = 8 Hz [24]. Hence, **8** was assigned the structure of spiro-(tricyclo[4.2.1.$0^{2,5}$]nonane- 3,3'-tetrahydroselenophene). Analogously, the structures of **7, 9, 10a**, and **10b** were proved.

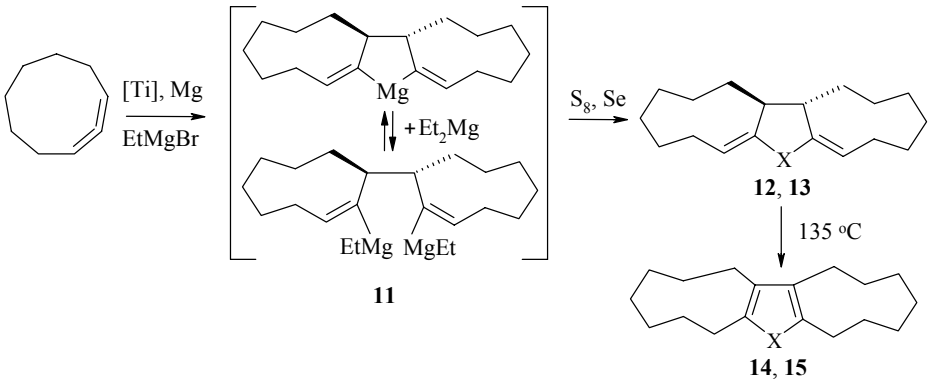
Scheme 2



To synthesize previously difficult to prepare tricyclic tetrahydrothiophenes symmetrically annelated with cycloalkenyl substituents, we studied the cyclomagnesation of 1,2-cyclononadiene by the action of EtMgBr in the presence of metallic magnesium (a halogen ion acceptor) and 5 mole % Cp_2TiCl_2 as catalyst in ether over 4 h at ~20°C, leading to 2-magnesatricyclo[10.7.$0^{1,12}$.$0^{3,11}$]nonadeca-3(4),19-diene (**11**) in ~90% yield (Scheme 3). The yields of the organometallic compounds were determined by gas-liquid chromatography of the products of their acid hydrolysis (see Experimental).

The cyclomagnesation of 1,2-cyclononadiene was complete after 3-4 h in ether. When the reaction was carried out in THF, the yield of magnesatricyclononadecadiene **11** did not exceed 8%. THF probably forms stronger complexes with the starting Grignard reagent in comparison with ether, which strongly reduces the reactivity of this reagent in the cyclomagnesation of 1,2-cyclononadiene.

Scheme 3



[Ti] = Cp_2TiCl_2; **12, 14** X = S; **13, 15** X = Se

The use of other Grignard reagents such as EtMgCl, EtMgI, *i*-PrMgBr, *p*-BuMgBr, and *i*-BuMgBr did not have any significant effect on the yield and composition of the cyclomagnesation products.

Tricyclic thiophane **12** and selenophane **13** are formed upon treating magnesatricyclononadecadiene **11** *in situ* with S_8 or Se. Upon heating to 135°C, products **12** and **13** are quantitatively converted into pure tricyclic thiophene **14** and selenophene **15**.

The ^{13}C NMR spectrum of **12** shows signals of nine nonequivalent carbon atoms. The downfield part of the spectrum shows a strong peak at δ = 120.1 ppm and a weak signal at δ = 142.5 ppm, corresponding to the signals of a trisubstituted double bond in the cyclononene fragment in the vinyl position to the sulfur atom.

The upfield part of the spectrum shows six signals at δ = 24-33 ppm and a signal for the nodal tertiary atom C-11 (δ = 51.9 ppm) at the fusion of the cyclononene and thiophane fragments as indicated by the Dept 135° spectra and the cross peak of this signal with the triplet of the proton H-4 at the double bond (δ = 5.41 ppm) in the HMBC experiment. The mass spectrum of compound **12** has a strong molecular ion peak M^+ 276.

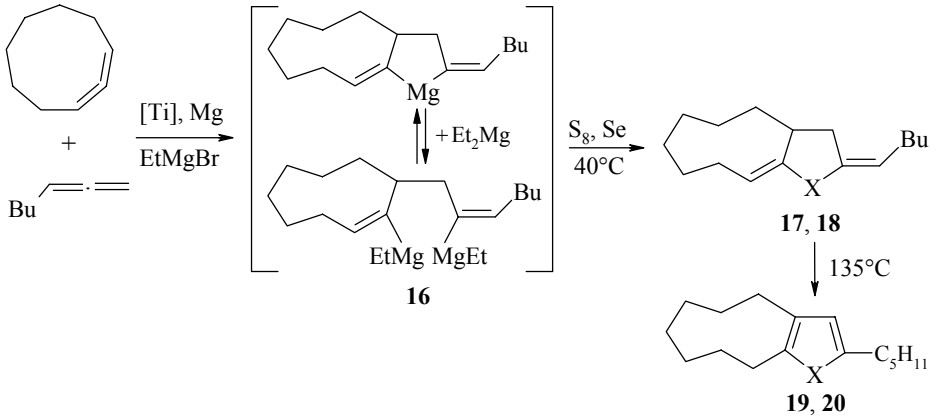
The ^{13}C NMR spectrum of compound **14** shows nine signals for nonequivalent carbon atoms. The downfield signals at δ = 135.6 and 137.5 ppm are assigned to the thiophene ring. The seven upfield signals for cyclononane fused to thiophene are found in a narrow range (δ = 24.3-29.4 ppm), indicating high molecular symmetry. The ^1H NMR spectrum shows a series of multiplets at δ = 1.2-1.8 ppm and two triplets for the methylene group protons at the vinyl position to the double bonds (δ = 2.59 and 2.83 ppm) with coupling constant J = 6 Hz.

The UV spectrum of compound **14** has a broad absorption band at 243 nm characteristic for tetrasubstituted thiophene. Thus, the spectral and elemental analysis data were used to identify compounds **12** and **14** as 2-thiatricyclo[10.7.$0^{1,12}$.$0^{3,11}$]nonadeca-3(4),19-diene and 2-thiatricyclo[10.7.$0^{1,12}$.$0^{3,11}$]nonadeca-1(12),3(11)-diene, respectively.

We then studied the combined cyclomagnesation of cyclic 1,2-dienes and acyclic allenes using Grignard reagents and Cp_2TiCl_2 as the catalyst. We assumed that the achievement of such a reaction would lead to the synthesis of bicyclic alkylidenemagnesacyclopentanes such as **16**, whose subsequent treatment *in situ* with S_8 and Se analogously to the scheme given above would lead to alkylidenetetrahydrothiophenes and the corresponding selenophenes, which have proved difficult to obtain in the past.

The achievement of these transformations in the cyclomagnesation of 1,2-cyclononadiene and 1,2-heptadiene by the action of EtMgBr in the presence of 5 mol % Cp_2TiCl_2 (the 1,2-cyclononadiene-1,2-heptadiene-EtMgBr-Mg-Cp_2TiCl_2 ratio was 10:10:40:24:1) in ether over 4 h at ~20°C led to the synthesis of bicyclic sulfur and selenium heterocycles **17-20** (Scheme 4).

Scheme 4

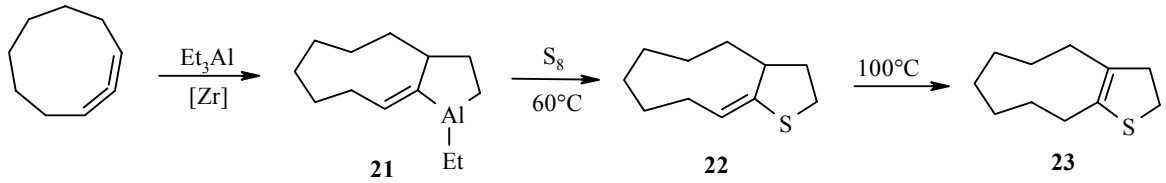


[Ti] = Cp_2TiCl_2; **17**, **19** X = S; **18**, **20** X = Se

The formation of the products of the homocyclomagnesation of 1,2-cyclononadiene and 1,2-heptadiene was observed in this reaction along with bicyclic alkylidenemagnesacyclopentane **16** in 1:1 ratio with a total yield of about 10%. However, only tricyclic thiophane **12** in 4-5% yield was found among the final products of the reaction of magnesacyclopentanes with S_8 along with the desired product **17**. Probably no 2,5-dialkylidene-thiophane is formed under these conditions as the result of the reaction of 2,5-dialkylidenemagnesacyclopentane with elemental sulfur.

In contrast to the cyclomagnesation of cyclic and acyclic 1,2-dienes, the catalytic cycloalumination of 1,2-cyclononadiene using $AlEt_3$ in the presence of Cp_2ZrCl_2 leads with high selectivity to bicyclic aluminacyclopentane **21** [25], whose reaction *in situ* with S_8 at 60°C gives 12-thiabicyclo[7.3.$0^{1,9}$]dodec-1(2)-ene (**22**) in high yield. Heating **22** at 100°C gives 12-thiabicyclo[7.3.$0^{1,9}$]dodec-1(9)-ene (**23**) in 98% yield (Scheme 5).

Scheme 5



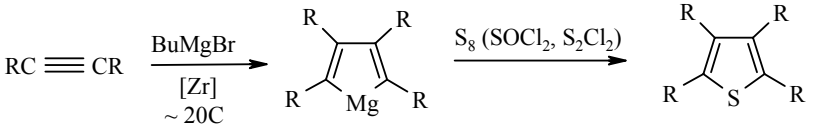
21 **22** **23**

[Zr] = Cp_2ZrCl_2

Having obtained extremely promising results for the synthesis of bicyclic and tricyclic thiophanes, thiophenes, selenophanes, and selenophenes by the homo- and mixed cyclomagnesation and cycloalumination of 1,2-cyclononadiene to give the corresponding magnesa- and aluminacyclopentanes, which were then converted by the action of S_8 or Se, we attempted to use this reaction for the homocyclometallation of 1,2-disubstituted acetylenes with the goal of developing a one-pot method for thiophene synthesis.

We selected 2,3,4,5-tetraalkylmagnesa-2,4-cyclopentadienes **24a**,**b** obtained *in situ* from 3-hexyne and 4-octyne under conditions reported in our previous work [26] and subjected these compounds to reaction with S_8, $SOCl_2$, and S_2Cl_2, which gave the corresponding 2,3,4,5-tetraalkylthiophenes **25a,b** in ~50% yield (Scheme 6).

Scheme 6



24a,b **25a,b**

24, 25 a R = Et, **b** R = Pr

Thus, the synthesis of five-membered sulfur and selenium heterocycles through a step involving the preparation *in situ* of five-membered organomagnesium and organoaluminum compounds by means of the Dzhemilev reaction is an efficient one-pot method for the construction of a variety of thiophanes, thiophenes, selenophanes, and selenophenes starting from methylenecycloalkanes, cyclic 1,2-dienes, and disubstituted acetylenes.

EXPERIMENTAL

The elemental analysis of the samples was carried out on a Carlo Erba 1106 analyzer. The electron impact mass spectra were taken on an MKh-1306 mass spectrometer at 70 eV and 200°C. The ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ on a Bruker Avance-400 spectrometer at 400 and 100 MHz, respectively. The yields of organomagnesium and organoaluminum compounds **4-6, 11, 16, 21,** and **24** were determined by gas-liquid chromatographic analysis of the hydrolysis products using *n*-hexadecane as the internal standard on a Chrom-5 chromatograph in a helium stream with a 1200×3-mm column packed with 5% SE-30 or 15% PEG on Chromaton N-AW. The reactions with the organometallic compounds were carried out in a stream of dry argon. Samples of THF and ether were dried by heating over metallic sodium at reflux. Commercial samples of 86% $EtAlCl_2$ and 99.8% $AlCl_3$ were used. The solutions of EtMgBr in THF and ether were prepared according to a standard procedure [27], while Cp_2ZrCl_2 was prepared from $ZrCl_4$ according to Nesmeyanov et al. [28].

Synthesis of Compounds 7-10 (General Method). Corresponding methylenecyclobutane derivative **1-3** (10 mmol), Cp_2ZrCl_2 (0.5 mmol), hexane (15 ml), and Et_3Al (12 mmol) were placed in a glass reactor in an atmosphere of dry argon at 0°C and stirred. The mixture was brought to ~20°C and stirring was continued for an additional 4 h to give **4-6**. Then, benzene (10 ml) and S_8 or Se (15 mmol) were added at 0°C and the mixture was heated for 6 h at 80°C. The reaction mixture was treated with 7-10% hydrochloric acid. The reaction products were extracted with hexane, dried over $MgSO_4$, and separated by vacuum distillation.

Spiro[tricyclo[4.2.1.0^{2,5}]nonane-3,3'-(tetrahydrothiophene)] (7) was obtained in 86% yield; bp 104-106°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.74-2.77 (2H, m, H-12); 2.78 (1H, d, *J* = 10, H-10); 2.53 (1H, d, *J* = 10, H-10); 2.16 (1H, m, H-5); 2.10 (1H, br. s, H-1); 1.98 (1H, br. s, H-6); 1.91-1.96 (2H, m, H-13); 1.88 (1H, d, *J* = 10, H-9); 1.79 (1H, d, *J* = 8, H-2); 1.52 (1H, dd, J_1 = 8, J_2 = 12, H-4); 1.50 (1H, dd, J_1 = 8, J_2 = 12, H-4); 1.44 (1H, m, H-8); 1.43 (1H, m, H-7); 1.20 (1H, d, *J* = 10, H-9); 0.99 (1H, m, H-8); 0.97 (1H, m, H-7). ^{13}C NMR spectrum, δ, ppm: 49.8 (C-2); 48.7 (C-3); 45.0 (C-4); 38.6 (C-5); 36.8 (C-6); 36.7 (C-1); 35.9 (C-10); 34.0 (C-9); 33.5 (C-13); 28.7 (C-7); 28.3 (C-12); 28.1 (C-8). Mass spectrum, *m/z* (I_{rel}, %): 194 $[M]^+$. Found, %: C 74.04; H 9.31; S 16.11. $C_{12}H_{18}S$. Calculated, %: C 74.16; H 9.34; S 16.50.

Spiro[tricyclo[4.2.1.0^{2,5}]nonane-3,3'-(tetrahydroselenophene)] (8) was obtained in 82% yield; bp 112-114°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.77-2.81 (2H, m, H-12); 2.62 (2H, d, *J* = 10, H-10); 2.13 (2H, m, H-1, H-5); 1.98-2.06 (2H, m, H-13); 1.99 (1H, br. s, H-6); 1.91 (1H, d, *J* = 10, H-9); 1.79 (1H, d, *J* = 8, H-2); 1.76 (1H, dd, J_1 = 8, J_2 = 12, H-4); 1.48 (1H, dd, J_1 = 8, J_2 = 12, H-4); 1.44 (1H, m, H-8); 1.43 (1H, m, H-7); 1.22 (1H, d, *J* = 10, H-9); 0.99 (1H, m, H-8); 0.98 (1H, m, H-7). ^{13}C NMR spectrum, δ, ppm: 50.2 (C-3); 49.6 (C-2); 46.7 (C-13); 38.6 (C-6); 36.7 (C-5); 36.6 (C-1); 34.2 (C-9); 33.5 (C-4); 29.0 (C-10); 28.8 (C-7); 28.1 (C-8); 20.3 C-12). Mass spectrum, *m/z* (I_{rel}, %): 194 $[M]^+$. Found, %: C 63.11; H 6.85; Se 29.64. $C_{12}H_{18}Se$. Calculated, %: C 63.39; H 6.84; Se 2.77.

Spiro[pentacyclo[5.4.0^{2,5}.0^{6,10}.0^{9,11}]undecane-3,3'-(tetrahydrothiophene)] (9) was obtained in 78% yield; bp 130-132°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.74-2.79 (2H, m); 2.80 (1H, d, *J* = 10); 2.56 (1H, d, *J* = 10); 2.29 (1H, m); 2.15 (1H, br. s); 1.98 (1H, br. s); 1.90 (1H, br. s); 1.88-2.01 (2H, m); 1.88 (1H, d, *J* = 10); 1.58 (1H, d, *J* = 8); 1.56 (1H, dd, J_1 = 8, J_2 = 12); 1.51 (1H, dd, J_1 = 8, J_2 = 12); 1.42 (1H, m); 1.08 (1H, d, *J* = 10); 0.76 (2H, m). ^{13}C NMR spectrum, δ, ppm: 49.3 (C-3); 48.8 (C-2); 46.0 (C-1); 44.4 (C-15); 43.1 (C-6); 37.6 (C-5); 36.6 (C-12); 36.3 (C-7); 34.1 (C-4); 31.7 (C-8); 28.4 (C-14); 13.8 (C-9, C-10); 12.9 (C-11). Mass spectrum, *m/z* (I_{rel}, %): 218 $[M]^+$. Found, %: C 76.84; H 8.29; S 14.72. $C_{14}H_{18}S$. Calculated, %: C 77.01; H 8.31; S 14.69.

A ~1:1 Mixture of Spiro[tetracyclo[5.4.1.0^{2,6}.0^{8,11}]dodec-3-ene-9,3'-(tetrahydrothiophene)] (10a) and Spiro[tetracyclo[5.4.1.0^{2,6}.0^{8,11}]dodec-4-ene-9,3'-tetrahydrothiophene)] (10b) was obtained in 81% yield; bp 141-144°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 5.56 (1H, m); 5.42 (1H, m); 2.19-3.0 (8H, m); 1.42-2.21 (10H, m). ^{13}C NMR spectrum, δ, ppm: 131.7 (C-3); 131.0 (C-4); 52.8 (C-2); 48.5 (C-9); 45.1 (C-8); 42.2 (C-7); 42.1 (C-1); 41.4 (C-16); 41.1 (C-6); 37.1 (C-10); 35.6 (C-12); 33.6 (C-13); 32.8 (C-5); 32.1 (C-11);

28.3 (C-15); 131.6 (C-4); 131.2 (C-5); 52.9 (C-6); 48.9 (C-9); 45.6 (C-2); 45.3 (C-1); 43.5 (C-16); 42.0 (C-7); 39.4 (C-8); 37.6 (C-10); 36.0 (C-13); 34.0 (C-12); 31.6 (C-11); 30.0 (C-3); 28.2 (C-15). Mass spectrum, *m/z* (I_{rel}, %): 232 $[M]^+$. Found, %: C 77.31; H 8.65; S 13.72. $C_{15}H_{20}S$. Calculated, %: C 77.53; H 8.67; S 13.80.

Synthesis of Compounds 12 and 13 (General Method). 1,2-Cyclononadiene (10 mmol), Cp_2TiCl_2 (0.5 mmol), magnesium powder (10 mmol), ether (10 ml), and EtMgBr (ethereal solution) (20 mmol) were added with stirring to a glass reactor in a dry argon atmosphere at 0°C. The mixture was brought to ~20°C and then stirred for 4 h to give compound **11**. Then, benzene (10 ml) and S_8 or Se (12 mmol) were added at 0°C and the mixture was heated for 6 h at 40°C. The reaction mixture was treated with 7-10% hydrochloric acid. The reaction products were extracted with hexane and dried over $MgSO_4$. The volatile solvents were removed in vacuum. The product was separated by column chromatography on a column packed with silica gel L (180/250 μ) using hexane as the eluent.

2-Thiatricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-3(4),19-diene (12) was obtained in 84% yield, R_f 0.45 (Silufol plate, hexane eluent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.41 (2H, dd, J_1 = 10.0, J_2 = 7.2, H-4, H-19); 2.71 (2H, m, H-11, H-12); 2.20 (4H, m, H-5, H-18); 1.61 (4H, m, H-10, H-13); 1.28-1.51 (16H, m). ^{13}C NMR spectrum, δ, ppm: 142.5 (C-1, C-3); 120.1 (C-4, C-19); 51.9 (C-11, C-12); 32.9 (C-10, C-13); 28.1 (C-5, C-18); 26.6 (C-6, C-17); 25.8 (C-7, C-16); 25.2 (C-8, C-15); 24.5 (C-9, C-14). Mass spectrum, *m/z* (I_{rel}, %): 276 $[M]^+$. Found, %: C 78.03; H 10.16; S 11.56. $C_{18}H_{28}S$. Calculated, %: C 78.19; H 10.21; S 11.60.

2-Selenatricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-3(4),19-diene (13) was obtained in 80% yield, R_f 0.43 (Silufol plate, hexane eluent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.29 (2H, t, *J* = 10, H-4, H-19); 2.79 (2H, m, H-11, H-12); 2.28 (4H, m, H-5, H-18); 1.58 (4H, m, H-10, H-13); 1.26-1.53 (16H, m). ^{13}C NMR spectrum, δ, ppm: 141.5 (C-1, C-3); 125.0 (C-4, C-19); 52.9 (C-11, C-12); 32.7 (C-10, C-13); 28.5 (C-5, C-18); 26.2 (C-6, C-17); 25.4 (C-7, C-16); 24.8 (C-8, C-15); 24.7 (C-9, C-14). Found, %: C 66.49; H 8.72; Se 24.39. $C_{18}H_{28}Se$. Calculated, %: C 66.86; H 8.73; Se 24.42.

Preparation of Compounds 14 and 15 (General Method). Diene **12** or **13** was placed in a glass ampule and heated for 6 h at 130°C to give compounds **14** or **15.** These products did not require further purification.

2-Thiatricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-1(12),3(11)-diene (14) was obtained in 82% yield, bp 180-182°C (1 mm Hg). UV spectrum, λ_{max}: 243 nm. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.83 (4H, t, *J* = 6.4, H-4, H-19); 2.59 (4H, t, *J* = 6.0, H-11, H-13); 1.68 (4H, m); 1.62 (4H, m); 1.48 (4H, m); 1.41 (8H, m). ^{13}C NMR spectrum, δ, ppm: 137.5 (C-1, C-3); 135.6 (C-11, C-12); 29.4 (C-4, C-19); 27.4 (C-10, C-13); 27.3 (C-5, C-18); 26.6 (C-6, C-17); 26.1 (C-7, C-16); 24.8 (C-8, C-15); 24.2 (C-9, C-14). Mass spectrum, *m/z* (I_{rel}, %): 276 $[M]^+$. Found, %: C 78.06; H 10.18; S 11.55. $C_{18}H_{28}S$. Calculated, %: C 78.19; H 10.21; S 11.60.

2-Selenatricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-1(12),3(11)-diene (15) was obtained in 95% yield, bp 191-193°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.91 (4H, t, *J* = 6, H-4, H-19); 2.55 (4H, t, *J* = 6, H-11, H-13); 1.68 (4H, m); 1.61 (4H, m); 1.49 (4H, m); 1.41 (8H, m). ^{13}C NMR spectrum, δ, ppm: 141.9 (C-1, C-3); 139.8 (C-11, C-12); 29.9 (C-4, C-19); 29.5 (C-10, C-13); 27.4 (C-5, C-18); 27.1 (C-6, C-17); 26.5 (C-7, C-16); 25.1 (C-8, C-15); 23.9 (C-9, C-14). Found, %: C 66.56; H 8.71; Se 24.43. $C_{18}H_{28}Se$. Calculated, %: C 66.86; H 8.73; Se 24.42.

Synthesis of Compounds 17 and 18 (General Method). 1,2-Cyclononadiene (10 mmol), 1,2-heptadiene (10 mmol), Cp_2TiCl_2 (1 mmol), magnesium powder (20 mmol), ether (10 ml), and EtMgBr (ethereal solution) (40 mmol) were added with stirring to a glass reactor in a dry argon atmosphere at 0°C. The mixture was then brought to ~20°C and stirred for 5 h to give compound **16**. Then, benzene (10 ml) and S_8 or Se (24 mmol) were added at 0°C and the mixture was heated at 40°C for 6 h. The reaction mixture was treated with 7-10% hydrochloric acid. The reaction products were extracted with hexane and dried over $MgSO_4$. The volatile solvents were removed in vacuum and the product was separated by chromatography on a column packed with silica gel L (180/250 μ) using hexane as the eluent.

11-(1-Pentylidene)-12-thiabicyclo[7.3.0^{1,9}]dodec-1(2)-ene (17) was obtained in 84% yield, R_f 0.46 (Silufol plate, hexane eluent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.41 (1H, t, *J* = 8.0, H-2); 5.28 (1H, t, *J* = 8.0, H-13); 2.84 (2H, d, *J* = 7.0, H-10); 2.52 (1H, m, H-9); 1.89 (6H, m); 1.32-1.49 (12H, m); 0.91 (3H, t, *J* = 6.0, 3-CH_3). ^{13}C NMR spectrum, δ, ppm: 142.3 (C-1); 139.7 (C-11); 123.2 (C-13); 120.5 (C-2); 50.8 (C-9); 36.4 (C-10); 32.9 (C-8); 32.2 (C-15); 30.9 (C-14); 28.4 (C-3); 26.8 (C-4); 25.8 (C-5); 25.3 (C-6); 24.4 (C-7); 22.3 (C-16); 13.8 (C-17). Mass spectrum, *m/z* (I_{rel}, %): 250 $[M]^+$. Found, %: C 76.61; H 10.41; S 12.81. $C_{16}H_{26}S$. Calculated, %: C 76.74; H 10.46; S 12.80.

11(1-Pentylidene)-12-selenabicyclo[7.3.0^{1,9}]dodec-1(2)-ene (18) was obtained in 81% yield, R_f 0.44 (Silufol plate, hexane eluent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.31 (1H, t, *J* = 8.0, H-2); 5.28 (1H, t, *J* = 8.0, H-13); 2.94 (2H, d, *J* = 7.0, H-10); 2.77 (1H, m, H-9); 1.91 (6H, m); 1,31-1.46 (12H, m); 0.92 (3H, t, *J* = 6.0, 3-CH_3). ^{13}C NMR spectrum, δ, ppm: 141.1 (C-1); 138.5 (C-11); 126.2 (C-13); 125.6 (C-2); 52.2 (C-9); 36.4 (C-10); 33.1 (C-8); 32.5 (C-15); 31.1 (C-14); 28.6 (C-3); 26.8 (C-4); 25.9 (C-5); 25.3 (C-6); 24.6 (C-7); 22.4 (C-16); 14.1 (C-17). Mass spectrum, *m/z* (I_{rel}, %): 297 $[M]^+$. Found, %: C 64.54; H 8.79; Se 26.60. $C_{16}H_{26}Se$. Calculated, %: C 64.63; H 8.81; Se 26.56.

Preparation of Compounds 19 and 20 (General Method). Dodecene **17** or **18** was placed in a glass ampule and heated for 8 h at 135-140°C to give compounds **19** or **20**.

11-Pentyl-12-thiabicyclo[7.3.0^{1,2}]dodeca-1(2),10(11)-diene (19) was obtained in 84% yield; bp 141-143°C (1 mm Hg). UV spectrum, λ_{max}: 236 nm. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.41 (1H, s, H-10); 2.80 (2H, t, *J* = 6.0, H-13); 2.71 (2H, t, *J* = 7.6, H-3); 2.62 (2H, t, *J* = 6.0, H-9); 1.65 (6H, m); 1.34-1.46 (10H, m); 0.92 (3H, t, *J* = 6.0, 3-CH_3). ^{13}C NMR spectrum, δ, ppm: 141.6 (C-1); 137.9 (C-11); 136.2 (C-2); 126.3 (C-10); 31.4 (C-12); 31.3 (C-14); 30.1 (C-9); 29.2 (C-3); 28.3 (C-13); 27.8 (C-6); 27.4 (C-8); 26.5 (C-5); 25.1 (C-4); 24.4 (C-7); 22.4 (C-15); 14.0 (C-16). Mass spectrum, *m/z* (I_{rel}, %): 250 $[M]^+$. Found, %: C 76.67; H 10.43; S 12.78. $C_{16}H_{26}S$. Calculated, %: C 76.74; H 10.46; S 12.80.

11-Pentyl-12-selenabicyclo[7.3.0^{1,2}]dodeca-1(2)-diene (20) was obtained in 81% yield; bp 152-154°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.59 (1H, s, H-10); 2.88 (2H, t, *J* = 6, H-13); 2.78 (2H, t, *J* = 7, H-3); 2.58 (2H, t, *J* = 6, H-9); 1.64 (6H, m); 1.35-1.47 (10H, m); 0.92 (3H, t, *J* = 6, 3-CH_3). ^{13}C NMR spectrum, δ, ppm: 148.5 (C-1); 142.7 (C-11); 139.6 (C-2); 129.3 (C-10); 32.8 (C-12); 32.2 (C-14); 31.3 (C-9); 29.6 (C-3); 29.4 (C-13); 28.7 (C-8); 27.8 (C-6); 26.4 (C-5); 25.0 (C-4); 24.6 (C-7); 22.4 (C-15); 14.0 (C-16). Mass spectrum, *m/z* (I_{rel}, %): 297 $[M]^+$. Found, %: C 64.39; H 8.83; Se 26.57. $C_{16}H_{26}Se$. Calculated, %: C 64.63; H 8.81; Se 26.56.

12-Thiabicyclo[7.3.0^{1,9}]dodec-1(2)-ene (22). 1,2-Cyclononadiene (10 mmol), Cp_2ZrCl_2 (0.5 mmol), hexane (15 ml), and Et_3Al (12 mmol) were added at 0°C with stirring to a glass reactor in a dry argon atmosphere. The mixture was brought to room temperature and stirred for 6 h. Then benzene (10 ml) and S_8 (15 mmol) were added at 0°C and the mixture was heated for 6 h at 60°C. The reaction mixture was treated with 7-10% hydrochloric acid. The reaction products were extracted with hexane and dried over $MgSO_4$. The volatile solvents were removed in vacuum. Dodecene **22** was an oil, which was separated on a chromatography column packed with silica gel L (180/250 μ) using hexane as the eluent. The yield of compound **22** was 69%, R_f 0.48 (Silufol plate, hexane eluent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.42 (1H, t, *J* = 7, H-2); 2.83 (2H, d, *J* = 9, H-11); 2.75 (1H, m, H-9); 2.20 (2H, m, H-3); 2.02 (2H, m, H-10); 1.61 (2H, m, H-8); 1.24-1.52 (8H, m). ^{13}C NMR spectrum, δ, ppm: 141.5 (C-1); 122.1 (C-2); 50.7 (C-9); 37.3 (C-10); 34.1 (C-11); 32.9 (C-8); 28.2 (C-3); 26.6 (C-6); 25.9 (C-5); 25.2 (C-4); 24.6 (C-7). Mass spectrum, *m/z* (I_{rel}, %): 182 $[M]^+$. Found, %: C 72.33; H 9.94; S 17.53. $C_{11}H_{18}S$. Calculated, %: C 72.46; H 9.95; S 17.59.

12-Thiabicyclo[7.3.0^{1,2}]dodec-1(2)-ene (23). Dodecene **22** was placed in a glass ampule and heated for 6 h at 100°C. Distillation gave dodecene **23** in 65% yield, bp 106-108°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.09 (2H, t, *J* = 8, H-11); 2.71 (2H, t, *J* = 8, H-10); 2.31 (2H, t, *J* = 6, H-9); 2.20 (2H, t, *J* = 6, H-3); 1.18-1.54 (8H, m). ^{13}C NMR spectrum, δ, ppm: 133.1 (C-1); 129.8 (C-9); 40.8 (C-10); 30.5 (C-11); 27.8 (C-8); 27.2 (C-2); 25.8 (C-6); 25.7 (C-5); 25.5 (C-4); 25.4 (C-3); 25.3 (C-7). Mass spectrum, *m/z* (I_{rel}, %): 182 $[M]^+$. Found, %: C 72.35; H 9.96; S 17.55. $C_{11}H_{18}S$. Calculated, %: C 72.46; H 9.95; S 17.59.

Synthesis of Tetraalkylthiophenes 25a and 25b (General Method). Unsubstituted acetylene (3-hexyne or 4-octyne) (10 mmol), Cp_2ZrCl_2 (1 mmol), ether (5 ml), and BuMgBr (20 mmol) (1.5 M ethereal solution) were added with stirring at 0°C to a glass reactor. The mixture was brought to room temperature and stirred for 2 h. Then, benzene (10 ml) and S_8 (24 mmol) were added at 0°C. The mixture was heated for 6 h at 40°C. When $SOCl_2$ or S_2Cl_2 are used, benzene is not required. The reaction mixture was cooled to -40°C and $SOCl_2$ or S_2Cl_2 (12 mmol) was added dropwise. The mixture was brought to room temperature, stirred for 4 h, and then treated with 7-10% hydrochloric acid. The reaction products were extracted with hexane, dried over $MgSO_4$, and separated by vacuum distillation.

2,3,4,5-Tetraethylthiophene (25a) was obtained in 50% yield; bp 74-76°C (3 mm Hg); 126-127°C (15.5 mm Hg) [29]. ^{1}H NMR spectrum, δ, ppm: 2.42-2.74 (8H, m, C$\underline{H_2}$CH$_3$); 0.98-1.11 (12H, m, 3-CH$_3$). ^{13}C NMR spectrum, δ, ppm: 136.1 (C-2, C-5); 134.9 (C-3, C-4); 23.2 (α-CH$_2$); 20.6 (β-CH$_2$); 12.4 (CH$_3$); 12.2 (CH$_3$). Mass spectrum, *m/z* (I_{rel}, %): 196 $[M]^+$. Found, %: C 73.26; H 10.25; S 16.09. $C_{12}H_{20}S$. Calculated, %: C 73.40; H 10.27; S 16.33.

2,3,4,5-Tetra(*n*-propyl)thiophene (25b) was obtained in 49% yield; bp 154-156°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 2.39-2.73 (8H, m, C$\underline{H_2}$CH$_3$); 1.22-1.67 (8H, m, C-CH$_2$-); 0.94-0.98 (12H, m, 3-CH$_3$). ^{13}C NMR spectrum, δ, ppm: 136.8 (C-2, C-5); 135.3 (C-3, C-4); 30.2 (CH$_2$); 29.3 (CH$_2$); 24.2 (CH$_2$); 21.9 (CH$_2$); 14.3 (CH$_3$); 13.5 (CH$_3$). Mass spectrum, *m/z* (I_{rel}, %): 252 $[M]^+$. Found, %: C 76.01; H 11.19; S 12.52. $C_{16}H_{28}S$. Calculated, %: C 76.12; H 11.18; S 12.70.

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REFERENCES

1. S. Gronowitz (editor), *Thiophene and its Derivatives*, Part 1, J. Wiley & Sons, New York (1985), p. 1.
2. L. I. Belen'kii, E. P. Zakharov, M. A. Kalik, V. P. Litvinov, F. M. Stoyanovich, S. Z. Taits, and B. P. Fabrichnyi, *New Directions in Thiophene Chemistry* [in Russian], Nauka, Moscow (1976), 424 pp.
3. L. I. Belen'kii, in: L. I. Belen'kii (editor), *Preparation and Properties of Organosulfur Compounds* [in Russian], Khimiya, Moscow (1998); p. 344.
4. Yu. K. Yur'ev, *Zh. Obshch. Khim.*, **6**, 1669 (1936).
5. Belg. Pat. 623801; *Chem. Abstr.*, **59**, 8705 (1963).
6. P. J. Fagan, W. A. Nugent, and J. C. Calabrese, *J. Am. Chem. Soc.*, **116**, 1880 (1994).
7. M. Mizza-Aghayan, R. Boukherroub, G. Etemad-Moghadam, G. Manuel, and M. Koenig, *Tetrahedron Lett.*, **37**, 3109 (1996).
8. M. Zablocka, A. Igau, B. Donnadieu, J. P. Majoral, A. Skowronska, and P. Meunier, *J. Chem. Soc., Chem. Commun.*, 1239 (1997).
9. Y. Miguel, A. Igau, B. Donnadieu, J. P. Majoral, N. Pirio, and P. Meunier, *J. Chem. Soc., Chem. Commun.*, 279 (1997).
10. U. M. Dzhemilev and A. G. Ibragimov, *J. Organomet. Chem.*, **466**, 1 (1994).
11. U. M. Dzhemilev and A. G. Ibragimov, *Izv. Akad. Nauk, Ser. Khim.*, 816 (1998).
12. U. M. Dzhemilev and A. G. Ibragimov, *Usp. Khim.*, **69**, 134 (2000).
13. U. M. Dzhemilev, *Tetrahedron*, **51**, 4333 (1995).
14. U. M. Dzhemilev and A. G. Ibragimov, *Usp. Khim.*, **74**, 886 (2005).
15. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1444 (1989).

16. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2831 (1990).
17. U. M. Dzhemilev, A. G. Ibragimov, A. B. Morozov, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1607 (1991).
18. U. M. Dzhemilev, A. G. Ibragimov, R. R. Gilyazev, and L. O. Khafizova, *Tetrahedron*, **60**, 1281 (2004).
19. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, L. M. Khalilov, and R. R. Muslukhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 386 (1992).
20. L. O. Khafizova, A. G. Ibragimov, G. N. Gil'fanova, L. M. Khalilov, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2089 (2001).
21. A. G. Ibragimov, L. O. Khafizova, G. N. Gil'fanova, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2095 (2002).
22. U. M. Dzhemilev, A. G. Ibragimov, L. O. Khafizova, L. P. Yakupova, and L. M. Khalilov, *Zh. Org. Khim.*, **40**, 684 (2004).
23. V. A. D'yakonov, E. Sh. Finkelshtein, and A. G. Ibragimov, *Tetrahedron Lett.*, **48**, 8583 (2007).
24. A. Gordon and R. Ford, *Chemist's Companion* [Russian translation], Mir, Moscow (1976), p. 301.
25. V. V. D'yakonov, R. K. Timerkhanov, A. G. Ibragimov, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2156 (2007).
26. U. M. Dzhemilev, A. G. Ibragimov, V. A. D'yakonov, and R. A. Zinnurova, *Zh. Org. Khim.*, **43**, 184 (2007).
27. S. T. Ioffe and A. M. Nesmeyanov, *Methods in Organoelement Chemistry. Magnesium, Beryllium, Calcium, Strontium, Barium Subgroup* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1963); p. 561.
28. R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR,* **138**, 1369 (1969).
29. P. Cagniant, *Bull. Soc. Chim. France*, 62 (1953).