molbank

MDPI

Communication

Modification of 1-Hexene Vinylidene Dimer into Primary and Tertiary Alkanethiols

Pavel V. Kovyazin *, Almira Kh. Bikmeeva, Eldar R. Palatov and Lyudmila V. Parfenova

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, Prospekt Oktyabrya, 141, 450075 Ufa, Russia; almira.bikmeeva@gmail.com (A.K.B.); kanohi@mail.ru (E.R.P.); luda_parfenova@ipc-ras.ru (L.V.P.)
* Correspondence: kpv38@mail.ru; Tel.: +7-347-284-3527

Abstract: Aliphatic thiols are in high demand in materials chemistry. Herein, a synthesis of thio-derivatives of 1-hexene vinylidene dimer is described. The approach, based on a hydroalumination reaction with further replacement of the organoaluminum function with sulfur using thiourea or dimethyl disulfide, provides anti-Markovnikov products, 2-butyloctane-1-thiol or 5-(methylsulfanylmethyl)undecane, in moderate yields. The reaction of a vinylidene dimer with phosphorus pentasulfide in the presence of catalytic amounts of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) selectively gives the Markovnikov product, 5-methylundecane-5-thiol, with a yield of up to 77%.

Keywords: vinylidene dimers; phosphorus pentasulfide; thiourea; dimethyl disulfide; thiols

check for updates

Citation: Kovyazin, P.V.; Bikmeeva, A.K.; Palatov, E.R.; Parfenova, L.V. Modification of 1-Hexene Vinylidene Dimer into Primary and Tertiary Alkanethiols. *Molbank* **2022**, *2022*, M1379. https://doi.org/10.3390/M1379

Academic Editor: Stefano D'Errico

Received: 28 April 2022
Accepted: 31 May 2022
Published: 4 June 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The focus on the development of methods for the synthesis of alkyl-substituted thiols Alk-SH is driven by the prospect of using these products as extractants of noble metals [1,2] and components of self-assembled monolayers [3–5], including the preparation and stabilization of AuNPs [6,7]. It was noted that the electronic and steric factors of the S-ligand largely determine the properties of the resulting nanoparticles [8].

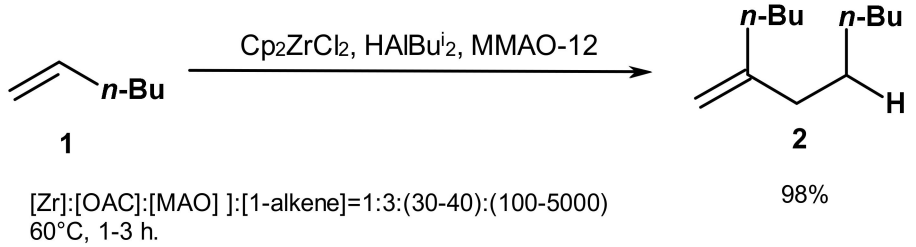
The literature describes a number of methods for the synthesis of aliphatic thiols from alkenes, alcohols, halogen derivatives, etc. [9–13]. Nevertheless, the high demand for this class of compounds has led to the search for new structures and approaches to their synthesis. Of particular interest is the utilization of terminal alkene dimers with a long branched hydrocarbon chain as an aliphatic component of thiols [14,15], which is viewed as a promising approach in materials chemistry. The present work is aimed at the study of 1-hexene dimer thiolation via hydrometalation and thiolene chemistry using P_2S_5 as a reagent.

2. Results and Discussion

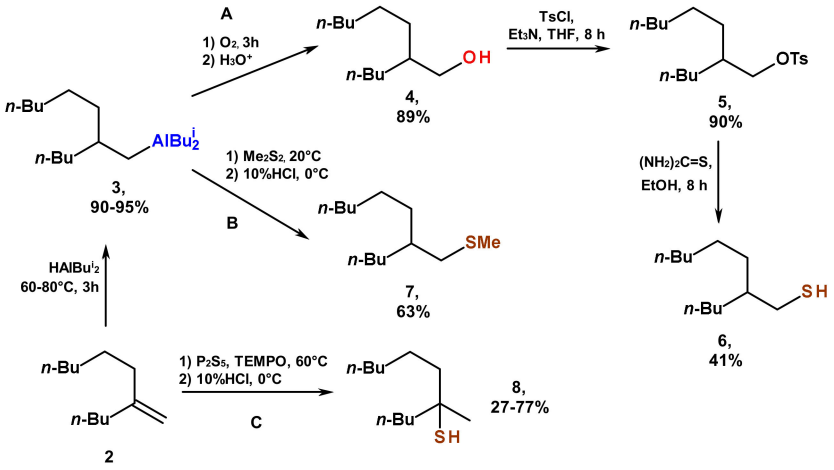
Previously, the conditions for the chemoselective synthesis of alkene dimers in systems based on zirconocenes, alkylalanes, and Al- or B-containing activators were determined [16–21]. It was shown that 1-hexene undergoes dimerization to give vinylidene dimer with a high yield and selectivity in the presence of a catalytic system of Cp_2ZrCl_2–$HAlBu^i_2$–MMAO-12 at a ratio of [Zr]:[Al]:[MMAO-12] = 1:3:30 and a temperature 60 °C (Scheme 1) [19].

Further, we searched for efficient methods of vinylidene dimer thiolation. Initially, a variant of the 1-hexene dimer functionalization by thermal hydroalumination and the subsequent conversion of the resulting organoaluminum compound into thio-derivatives was considered (Scheme 2, routes **A** and **B**). The heating between 60 and 80 °C of an equimolar mixture of vinylidene dimer **2** and $HAlBu^i_2$ in toluene for 3 h gave a hydroalumination product **3** with a yield of 90–95% (determined by GC/MS of hydrolysis or deuterolysis

products of the reaction mixture). As a result of bubbling the reaction mixture with oxygen for 1 h with additional stirring in an O_2 atmosphere for 3 h, alcohol **4** was obtained with a yield of 80–89% (route A). The reaction of **4** with P_2S_5 in toluene gave product **6** with a very low yield (Table 1, entry 1). Further transformations of **4** were carried out in accordance with the method described in [12]. Thus, the alcohol **4** was converted into tosylate **5**. The reaction of **5** with thiourea in ethanol for 8 h provided thiol **6** with a yield of up to 41% (entry 2).



Scheme 1. Dimerization of 1-hexene in the presence of catalytic system of Cp_2ZrCl_2–$HAlBu^i_2$–MMAO-12.



Scheme 2. Methods for 1-hexene dimer thiolation.

As an alternative method, the replacement of an aluminum atom in the organoaluminum compound with a sulfur atom was considered [22,23]. For this purpose, the reactions of OAC **3**, obtained in situ, with dimethyl disulfide $(MeS)_2$, thiourea $(H_2N)_2C{=}S$, and P_2S_5 were studied (route **B**). The reactions of **3** with $(H_2N)_2C{=}S$ and P_2S_5, followed by thehydrolysis of the reaction mixture, gave the thiolated product **6** in a yield of no more than 5% (entries 3, 4). OAC **3** was reacted with Me_2S_2 at room temperature for 16 h to give thioether R-SMe (7) with a yield of up to 63% (entry 5).

The further search for synthetic ways to S-modify alkene dimers led to the development of a method based on the reaction of vinylidene dimer with P_2S_5 at a ratio of 1:1 in the presence of 0.8 mol% TEMPO (entries 7–16). In this case, the Markovnikov product, tertiary thiol **8**, was formed with a yield of up to 77% (entry 7). Reducing the amount of P_2S_5 to 0.5 eq. or using other solvents decreases the product yield.

In summary, studied various methods for the preparation of alkene dimer thioderivatives. Dimer hydrometalation followed by reactions of oxidized product or OAC with thiourea or dimethyl disulfide provides anti-Markovnikov products, alkylthiol or methylalkyl sulfide, in moderate yields. The reaction of 1-hexene dimer with P_2S_5 in the presence of catalytic amounts of TEMPO leads to the selective formation of tertiary thiol, with yields of up to 77%.

Table 1. Conditions for the synthesis of S-functionalized derivatives of dimer 2.

Entry	Substrate	OAC	Solvent	Thiolation Reagent	Substrate:HAlBu $^{i}_{2}$:Reagent	t, °C	Time, h	Product, Yield
1	**4**		toluene	P_2S_5	1:0:1	60	16	**6**, <3%
2	**5**		EtOH	$(H_2N)_2C=S$	1:0:1	60	8	**6**, 41%
3	**2**	$HAlBu^{i}_{2}$	toluene	$(H_2N)_2C=S$	1:1:(1–3)	80	16	
4	**2**	$HAlBu^{i}_{2}$	toluene	P_2S_5	1:1:(1–3)	60	16	**6**, <5%
5	**2**	$HAlBu^{i}_{2}$	toluene	Me_2S_2	1:1:(1–3)	20	16	**7**, 63%
6	**2**		toluene	P_2S_5	1:0:1	80	16	
7	**2**		toluene	P_2S_5 [a]	1:0:1	60	16	**8**, 77%
8	**2**		toluene	P_2S_5 [a]	1:0:0.5	60	16	**8**, 40%
9	**2**		hexane	P_2S_5 [a]	1:0:1	60	16	**8**, 37%
10	**2**		$CHCl_3$	P_2S_5 [a]	1:0:1	60	16	**8**, 29%
11	**2**		CH_2Cl_2	P_2S_5 [a]	1:0:1	20	16	**8**, 41%
12	**2**		Et_2O	P_2S_5 [a]	1:0:1	20	16	**8**, 33%
13	**2**		THF [b]	P_2S_5 [a]	1:0:1	60	16	**8**, 27% [b]
14	**2**		H_2O	P_2S_5 [a]	1:0:1	60	16	**8**, 30%
15	**2**		10% HCl	P_2S_5 [a]	1:0:1	60	16	**8**, 54%
16	**2**		EtOH	P_2S_5 [a]	1:0:1	60	16	**8**, 9%

[a] The reaction was carried out in the presence of 0.8 mol% TEMPO. [b] The products of oxygen atom substitution in THF molecule by sulfur and thiophane (35%), and the products of the ring opening, 1,4-dithiol (12%), were identified by GC/MS.

3. Materials and Methods

General Procedures

All operations for organometallic compounds were performed under argon, according to Schlenk technique. The solvents ($CHCl_3$ and CH_2Cl_2) were distilled from P_2O_5 immediately prior to use. The solvents (toluene, hexane, THF, and Et_2O) were distilled from CaH_2 immediately prior to use. Commercially available P_2S_5 (99%, Merck KGaA, Darmstadt, Germany), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (98%, Acros, Geel, Belgium), Me_2S_2 (99%, Acros), $HAlBu^{i}_{2}$ (99%, Merck), $(H_2N)_2C=S$ (99%, Acros), TsCl (99%, Acros), and Et_3N (99%, Merck) were used. CAUTION: pyrophoric nature of aluminum alkyl and hydride compounds means that they require special safety precautions in their handling.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (1H), 100.62 MHz (^{13}C)) (Bruker, Rheinstetten, Germany). $CDCl_3$ was employed as the solvent and the internal standard. 1D and 2D NMR spectra (COSY HH, HSQC, HMBC) were recorded using standard Bruker pulse sequences.

The products were analyzed using a gas chromatograph-mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Tokyo, Japan) equipped with the GC-2010 Plus chromatograph (Shimadzu, Tokyo, Japan), TD-20 thermal desorber (Shimadzu, Tokyo, Japan), and an ultrafast quadrupole mass-selective detector (Shimadzu, Tokyo, Japan).

Synthesis of Compound **4.** A flask with a magnetic stirrer was filled under argon with 1.0 g (5.6 mmol) of dimer **2**, 1.0 mL (5.6 mmol) of $HAlBu^{i}_{2}$, and 2 mL of toluene. The reaction was carried out through stirring at 60 °C. After 3 h, the reaction mixture was cooled to 0 °C and dry oxygen was passed through the mixture for 1 h. The resultant mixture was further stirred in oxygen atmosphere for 3 h, and then treated with 10% HCl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. The products were analyzed by GC/MS. The crude product was air-dried and purified by flash chromatography over silica gel (0.060–0.200 mm 60 A, eluent: petroleum ether/Et_2O = 7/1). Yield 0.92 g (89%). δ_H (400 MHz, $CDCl_3$) 0.79–1.02 (m, 6H, CH_3); 1.16–1.44 (m, 16H, CH_2); 1.38–1.55 (m, 1H, CH); 3.55 (d, 2H, J = 5.3 Hz, CH_2OH) (Figure S1). δ_C (100.13 MHz, $CDCl_3$) 14.1 (CH_3); 22.7, 23.1, 26.9, 29.1, 29.7, 31.9 (CH_2); 30.6, 30.9 (CH_2CH); 40.5, (CH); 65.7 (CH_2OH) (Figure S2). m/z (I, %) [M-H_2O] = 168 (2), 154 (2), 140 (3), 139 (1), 126 (5), 125 (7), 124 (1), 113 (4), 112 (8), 111 (22), 110 (4), 99 (10), 98 (12), 97 (20), 96 (5), 85 (36), 84 (21), 83 (22), 71 (46), 70 (29), 65 (36), 57 (100).

Synthesis of Compound **5**. A flask with a magnetic stirrer was filled under argon at 0 °C with 0.9 g (4.9 mmol) of **2**, 1.7 g (5.4 mmol) of TsCl, 25 mL of dry THF and 1.0 mL (7.4 mmol) of freshly distilled Et_3N. The reaction was carried out through stirring at 20 °C for 8 h, and then treated with 10% HCl and extracted with CH_2Cl_2. The organic layer was dried

over Na_2SO_4, filtered, and concentrated to give 1.51 g (90%) of tosylate **5**. δ_H (400 MHz, $CDCl_3$) 0.76–0.96 (m, 6H, CH_3); 0.98–1.68 (m, 16H, CH_2); 1.50–1.65 (m, 1H, CH); 3.91 (d, 2H, J = 5.1 Hz, CH_2OH), 2.48 (s, 3H, CH_3Ph), 7.34 (d, 2H, J = 7.8 Hz, Ph), 7.78 (d, 2H, J = 7.8 Hz, Ph) (Figure S3). δ_C (100.13 MHz, $CDCl_3$) 14.0, 14.1 (CH_3); 22.6, 22.8, 26.4, 28.6, 29.5, 31.7 (CH_2); 30.3, 30.6 (CH_2CH); 37.6 (CH); 72.8 (CH_2OH); 21.6 (CH_3Ph); 129.8, 130.3, 133.1, 146.9 (Ph) (Figure S4). m/z (I, %) [M-O_2SPhMe] = 187 (3), 173 (31), 172 (10), 169 (7), 168 (46), 155 (31), 140 (11), 126 (22), 125 (21), 112 (28), 111 (71), 110 (14), 98 (45), 97 (42), 92 (26), 91 (100).

Synthesis of Compound **6.** Thiourea (0.4 g, 5.4 mmol) was added in portions to a solution of 1.5 g (4.4 mmol) tosylate **5** in ethanol. The reaction was carried out through stirring at room temperature for 8 h, and then treated with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography over silica gel (0.060–0.200 mm 60 A, eluent: petroleum ether). Yield 0.37 g (41%). The NMR data corresponded to those reported in the literature [14]. m/z (I, %) [M] = 202 (12), 203 (2), 168 (15), 145 (2), 140 (4), 126 (5), 125 (10), 117 (2), 113 (4), 112 (7), 111 (20), 110 (5), 99 (8), 98 (11), 97 (17), 96 (4), 85 (31), 84 (17), 83 (22), 82 (7), 71 (45), 70 (27), 69 (37), 57 (100).

Synthesis of Compound **7.** A flask with a magnetic stirrer was filled under argon with 200 mg (1.2 mmol) of dimer **2**, 0.2 mL (1.2 mmol) of $HAlBu^i_2$, and 2 mL of toluene. The reaction was carried out through stirring at 60 °C. After 3 h, 0.1–0.3 mL (1.2–3.6 mmol) of Me_2S_2 was added to the reaction mixture at 0 °C and stirred for 16 h at 20 °C. The mixture was then decomposed with 10% HCl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. The products were analyzed by GC/MS. The crude product was air-dried and purified by flash chromatography over silica gel (0.060–0.200 mm 60 A, eluent: petroleum ether) to give 162 mg (63%) of **7**. δ_H (400 MHz, $CDCl_3$) 0.790–0.99 (6H, CH_3); 2.10 (s, 3H, CH_3S); 2.49 (d, 2H, J = 6.3 Hz, CH_3SCH_2CH), 1.46–1.53 (1H, CH), 1.04–1.51 (16H, CH_2) (Figure S5). δ_C (100.13 MHz, $CDCl_3$) 14.1 (CH_3); 16.3 (CH_3S) 22.7, 23.0, 26.6, 28.8, 29.7, 31.9 (CH_2); 32.9 ($CHCH_2(CH_2)_2CH_3$); 33.2 ($CH_3(CH_2)_4CH_2CH$); 37.6 (CH); 39.6 ($CHCH_2SCH_3$) (Figure S6). m/z (I, %) [M] = 216 (65), 218 (4), 217 (11), 203 (1), 202 (4), 201 (25), 169 (1), 168 (11), 159 (3), 145 (1), 131 (3), 127 (1), 126 (11), 125 (15), 124 (3), 112 (16), 111 (45), 110 (11), 99 (8), 98 (30), 97 (39), 96 (10), 85 (21), 84 (38), 83 (45), 82 (13), 81 (6), 71 (33), 70 (61), 69 (67), 62 (21), 61 (54), 57 (87), 56 (65), 55 (76), 43 (100).

Synthesis of Compound **8.** A flask with a magnetic stirrer was filled under argon with 264 mg (1.2 mmol) of P_2S_5, 200 mg (1.2 mmol) of dimer **2**, 1.5 mg (0.0095 mmol) of TEMPO, and 2 mL of solvents (toluene, hexane, $CHCl_3$, CH_2Cl_2, THF, Et_2O, H_2O, and EtOH). The reaction was carried out with stirring at temperatures between 20 and 80 °C. After 8–24 h, the reaction mixture were decomposed with 10% HCl at 0 °C. Products were extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4. The products were analyzed by GC/MS. The crude product was-air dried and purified by flash chromatography over silica gel (0.060–0.200 mm 60 A, eluent: petroleum ether) to give 186 mg (77%) of **8**. δ_H (400 MHz, $CDCl_3$) 0.79–1.01 (6H, CH_3); 1.30–1.69 (4H, CH_2CCH_2); 0.99–1.69 (15H, CH_2, CCH_3) (Figure S7). δ_C (100.13 MHz, $CDCl_3$) 14.1 (CH_3); 22.7, 23.1, 24.74, 27, 30.3, 31.8 (CH_2); 29.7 (CH_3C); 44.05, 44.33 (CH_2CCH_2); 48.3 (CSH) (Figure S8). m/z (I, %) [M] = 202 (3), 170 (4), 145 (9), 127 (5), 126 (2), 118 (1), 117 (17), 116 (2), 114 (1), 113 (13), 112 (2), 111 (13), 110 (1), 99 (20), 98 (4), 97 (4), 87 (2), 86 (3), 85 (44), 84 (6),83 (27), 82 (2), 81 (2), 79 (2), 77 (1), 75 (5), 74 (8), 72 (4), 71 (64), 70 (15), 69 (47), 68 (3), 67 (5), 65 (1), 61 (12), 59 (6), 58 (5), 57 (100).

Supplementary Materials: The following supporting information at: Figures S1–S8: NMR spectra of **4**, **5**, **7**, **8**.

Author Contributions: Conceptualization, L.V.P.; methodology, P.V.K. and A.K.B.; validation, L.V.P., P.V.K.; formal analysis, P.V.K., A.K.B., and E.R.P.; investigation, P.V.K., A.K.B., and E.R.P.; resources, P.V.K. and L.V.P.; data curation, P.V.K. and L.V.P.; writing—original draft preparation, P.V.K. and L.V.P.; writing—review and editing, L.V.P.; visualization, P.V.K.; supervision, L.V.P.; project administration, P.V.K.; funding acquisition, P.V.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Russian Science Foundation, grant number 19-73-10122.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors acknowledge the use of equipment in the Agidel Collective Use Centre at the Institute of Petrochemistry and Catalysis of RAS, FMRS-2022-0081.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pronin, V.A.; Usol'tseva, M.V.; Trofimov, B.A.; Vyalykh, E.P.; Shastina, Z.N. Extractive power of certain mercaptans with respect to Au (III), Ag (I), Pt (IV), and Pd (II). *J. Appl. Chem. USSR* **1973**, *46*, 2758–2760.
2. Chen, D.; Cui, P.; Cao, H.; Yang, J. A 1-dodecanethiol-based phase transfer protocol for the highly efficient extraction of noble metal ions from aqueous phase. *J. Environ. Sci.* **2015**, *29*, 146–150. [CrossRef] [PubMed]
3. Holmlin, R.E.; Haag, R.; Chabinyc, M.L.; Ismagilov, R.F.; Cohen, A.E.; Terfort, A.; Rampi, M.A.; Whitesides, G.M. Electron Transport through Thin Organic Films in Metal−Insulator−Metal Junctions Based on Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2001**, *123*, 5075–5085. [CrossRef] [PubMed]
4. Urcuyo, R.; Cortés, E.; Rubert, A.A.; Benitez, G.; Montero, M.L.; Tognalli, N.G.; Fainstein, A.; Vela, M.E.; Salvarezza, R.C. Aromatic and Aliphatic Thiol Self-Assembled Monolayers on Au: Anchoring and Delivering Copper Specie. *J. Phys. Chem. C* **2011**, *115*, 24707–24717. [CrossRef]
5. Denayer, J.; Delhalle, J.; Mekhalif, Z. Comparative study of copper surface treatment with self-assembled monolayers of aliphatic thiol, dithiol and dithiocarboxylic acid. *J. Electroanal. Chem.* **2009**, *637*, 43–49. [CrossRef]
6. Goswami, N.; Yao, Q.; Chen, T.; Xie, J. Mechanistic exploration and controlled synthesis of precise thiolate-gold Nanoclusters. *Coord. Chem. Rev.* **2016**, *329*, 1–15. [CrossRef]
7. Yeh, Y.-C.; Creran, B.; Rotello, V.M. Gold nanoparticles: Preparation, properties, and applications in bionanotechnology. *Nanoscale* **2012**, *4*, 1871–1880. [CrossRef]
8. Rambukwella, M.; Sakthivel, N.A.; Delcamp, J.H.; Sementa, L.; Fortunelli, A.; Dass, A. Ligand Structure Determines Nanoparticles' Atomic Structure, Metal-Ligand Interface and Properties. *Front. Chem.* **2018**, *6*, 330. [CrossRef]
9. Wardell, J.L. Preparation of thiols. In *The Thiol Group*; Patai, S., Ed.; John Wiley & Sons Ltd: Bristol, UK, 1974. [CrossRef]
10. Hoyle, C.; Bowman, C. Thiol–Ene Click Chemistry. *Angew. Chem. Int. Ed.* **2010**, *49*, 1540–1573. [CrossRef]
11. Lowe, A.B. Thiol-ene "click" reactions and recent applications in polymer and materials synthesis. *Polym. Chem.* **2010**, *1*, 17–36. [CrossRef]
12. Snow, A.W.; Foos, E.E. Conversion of Alcohols to Thiols via Tosylate Intermediates. *Synthesis* **2003**, *4*, 509–512. [CrossRef]
13. Maurya, C.K.; Gupta, P.K. Phosphorus Pentasulfide Mediated Conversion of Primary Carbamates into Thiols. *Synlett* **2017**, *28*, 1649–1651. [CrossRef]
14. Nifant'ev, I.; Ivchenko, P.; Tavtorkin, A.; Vinogradov, A.; Vinogradov, A. Non-traditional Ziegler-Natta Catalysis in a-Olefin Transformations: Reaction Mechanisms and Product Design. *Pure Appl. Chem.* **2017**, *89*, 1017–1032. [CrossRef]
15. Nifant'ev, I.; Ivchenko, P. Fair Look at Coordination Oligomerization of Higher α-Olefins. *Polymers* **2020**, *12*, 1082. [CrossRef]
16. Nifant'ev, I.E.; Vinogradov, A.A.; Vinogradov, A.A.; Ivchenko, P.V. Zirconocene-Catalyzed Dimerization of 1-Hexene: Two-stage Activation and Structure–Catalytic Performance Relationship. *Cat. Comm.* **2016**, *79*, 6–10. [CrossRef]
17. Nifant'ev, I.E.; Vinogradov, A.A.; Vinogradov, A.A.; Sedov, I.V.; Dorokhov, V.G.; Lyadov, A.S.; Ivchenko, P.V. Structurally Uniform 1-Hexene, 1-Octene, and 1-Decene Oligomers: Zirconocene/MAO-Catalyzed Preparation, Characterization, and Prospects of Their Use as low-viscosity Low-temperature Oil Base Stocks. *Appl. Catal. A Gen.* **2018**, *549*, 40–50. [CrossRef]
18. Nifant'ev, I.; Vinogradov, A.; Vinogradov, A.; Karchevsky, S.; Ivchenko, P. Experimental and Theoretical Study of Zirconocene-Catalyzed Oligomerization of 1-Octene. *Polymers* **2020**, *12*, 1590. [CrossRef]
19. Parfenova, L.V.; Kovyazin, P.V.; Bikmeeva, A.K. Bimetallic Zr,Zr-Hydride Complexes in Zirconocene Catalyzed Alkene Dimerization. *Molecules* **2020**, *25*, 2216. [CrossRef]
20. Parfenova, L.V.; Kovyazin, P.V.; Bikmeeva, A.K.; Palatov, E.R. Catalytic Systems Based on Cp_2ZrX_2 (X = Cl, H), Organoaluminum Compounds and Perfluorophenylboranes: Role of Zr,Zr- and Zr,Al-Hydride Intermediates in Alkene Dimerization and Oligomerization. *Catalysts* **2021**, *11*, 39. [CrossRef]
21. Kovyazin, P.V.; Bikmeeva, A.K.; Islamov, D.N.; Yanybin, V.M.; Tyumkina, T.V.; Parfenova, L.V. Ti subgroup metallocene-catalyzed synthesis of 1-hexene dimers and tetramers. *Molecules* **2021**, *26*, 2775. [CrossRef]
22. Dzhemilev, U.M.; Ibragimov, A.G.; Zolotarev, A.P.; Tolstikov, G.A. Nontraditional approach to the synthesis of 3-substituted tetrahydrothiophenes and tetrahydroselenophenes. *Russ. Chem. Bull.* **1989**, *38*, 1324. [CrossRef]
23. Dzhemilev, U.M.; Ibragimov, A.G.; Azhgaliev, M.N.; Muslukhov, R.R. Synthesis and transformations of metallocycles. *Russ. Chem. Bull.* **1994**, *43*, 255–257. [CrossRef]