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Facile Synthesis of (Imido)vanadium(V)−Alkyl, Alkylidene Complexes Containing an N-Heterocyclic Carbene Ligand from Their Trialkyl Analogues

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Summary: (Imido)vanadium(V)−alkyl, alkylidene complexes containing an N-heterocyclic carbene (NHC) ligand, $V(CHSiMe_3)(NR)(CH_2SiMe_3)(NHC)$ [R = 1-adamantyl (Ad) or $2,6\text{-}Me_2C_6H_3$ (Ar), NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], have been prepared from the trialkyl analogues, $V(NR)(CH_2SiMe_3)_3$, by α-hydrogen elimination in C_6D_6 in the presence of NHC. The V−C(NHC) bond distance [2.172(2) Å] in $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(NHC)$ is much longer than the V−C(alkylidene) [1.829 Å] and the V−C(alkyl) [2.069 Å] distances, indicating that NHC plays an important role in the stabilization of the high-oxidation-state vanadium(V)−alkylidene as a neutral carbene ligand.

High-oxidation-state early transition metal alkylidene complexes attract considerable attention[1] because they play essential roles as catalysts in olefin metathesis and Wittig-type group transfer reactions,[1,2] as demonstrated by molybdenum.[1a−d,2] Although classical Ziegler-type vanadium catalysts displayed unique characteristics in olefin coordination insertion polymerization (notable reactivity toward olefins),[3,4] examples with vanadium(V)−alkylidenes still have been limited.[1e,f,5−7] We recently introduced that (arylimido)vanadium(V)−alkylidene complexes containing ketimide[6b,e] and aryloxo[6d] ligands exhibited high catalytic activities for ring-opening metathesis polymerization of norbornene. Although titanium(IV)−alkyl, alkylidene complexes display unique reactivities with various organic compounds via a "$Ti{\equiv}C^{t}Bu$" intermediate,[8] synthesis and the reaction chemistry of the vanadium(V)-alkyl, alkylidene complexes have not been reported so far.[9] We thus herein present that syntheses of (imido)vanadium(V)−alkyl, alkylidene complexes, $V(CHSiMe_3)(NR)(CH_2SiMe_3)(NHC)$ [R = 1-adamantyl (Ad), $2,6\text{-}Me_2C_6H_3$ (Ar); NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], have been achieved from the trialkyl analogues by α-hydrogen abstraction in the presence of NHC.[10]

Reaction of $V(NAd)Cl_3$ prepared by the reported method[11] with 3.0 equiv of $LiCH_2SiMe_3$ in *n*-hexane gave the trialkyl analogue $V(NAd)(CH_2SiMe_3)_3$ (**1**) in moderate yield (64%), and the procedure is analogous to that for synthesis of the arylimido analogue $V(NAr)(CH_2SiMe_3)_3$ (**2**).[6d] Complex **1** was identified on the basis of NMR spectra and elemental analysis, and the structure was determined by X-ray crystallography (Figure 1).[10] Complex **1** has a rather distorted tetrahedral geometry around V, and the V−N−C bond angle is 180.00(17)° and the V−N distance is 1.6317(14) Å; the results would be a unique contrast to those in $V(N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)(CH_2Ph)_3$ [V−N−C 169.0(5)° and 1.641(6) Å].[12] The three V−C bond distances and angles are

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(1) For examples, see: (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Schrock, R. R. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, Germany, 1998; p 1. (c) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (d) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, p 8. (e) Mindiola, D. *Acc. Chem. Res.* **2006**, *39*, 813. (f) Mindiola, D.; Bailey, B.; Basuli, F. *Eur. J. Inorg. Chem.* **2006**, *16*, 3135.

(2) For examples, see: (a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vols. 1−3. (c) Khosravi, E., Szymanska-Buzar, T., Eds. *Ring-Opening Metathesis Polymerisation and Related Chemistry*; Kluwer: Dordrecht, The Netherlands, 2002. (d) Imamoglu, Y., Dragutan, V., Eds. *Metathesis Chemistry*; Springer: Dordrecht, The Netherlands, 2007.

(3) Examples: (a) Carrick, W. L. *J. Am. Chem. Soc.* **1958**, *80*, 6455. (b) Carrick, W. L.; Kluiber, R. W.; Bonner, E. F.; Wartman, L. H.; Rugg, F. M.; Smith, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3883. (c) Carrick, W. L.; Reichle, W. T.; Pennella, F.; Smith, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 3887. (d) Lehr, M. H. *Macromolecules* **1968**, *1*, 178.

(4) For reviews, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (c) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (d) Nomura, K. In *New Developments in Catalysis Research*; Bevy, L. P., Ed.; NOVA Science Publishers: New York, 2005; p 199.

(5) Examples for isolation of terminal vanadium(III),(IV) alkylidenes:[1e,f] (a) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 5977. (b) Hessen, B.; Meetsma, A.; Van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925. (c) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156. (d) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506.

(6) Examples for terminal vanadium(V)−alkylidenes: (a) Buijink J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922. No reaction between $CpV(CHPh)(NAr)(PMe_3)$ and norbornene or acetone was observed. (b) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2005**, *24*, 2248. (c) Kilgore, U. J.; Sengelaub, C. A.; Pink, M.; Fout, A. R.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 3769. No descriptions concerning application as the catalysts. (d) Nomura, K.; Onishi, Y.; Fujiki, M.; Yamada, J. *Organometallics* **2008**, *27*, 3818. (e) Zhang, W.; Yamada, J.; Nomura, K. *Organometallics*, **2008**, *27*, 5353.

(7) Examples for related complexes containing vanadium(V)−carbon double bonds: (a) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1990**, *9*, 1925. (b) Moore, M.; Gambarotta, S.; Yap, G.; Liable-Sands, L. M.; Rheingold, A. L. *Chem. Commun.* **1997**, 643.

(8) (a) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16016. (b) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 6798. (c) Bailey, B. C.; Fout, A. R.; Fan, H.; Tomaszweski, J.; Huffman, J. C.; Gary, J. B.; Johnson, M. J. A.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 2234. (d) Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 5302. (e) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 8781. (f) Fout, A. R.; Bailey, B. C.; Tomaszweski, J.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 12640.

(9) Synthesis of vanadium(IV)−alkyl, alkylidene yielding terminal vanadium(V)−neopentylidyne upon addition of AgOTf (Tf = CF_3SO_2). Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506.

(10) Experimental details including syntheses, identification, and structural analysis reports are shown in the Supporting Information.

(11) Zhang, W.; Nomura, K. *Inorg. Chem.* **2008**, *47*, 6482.

(12) Murphy, V. J.; Turner, H. *Organometallics* **1997**, *16*, 2495.

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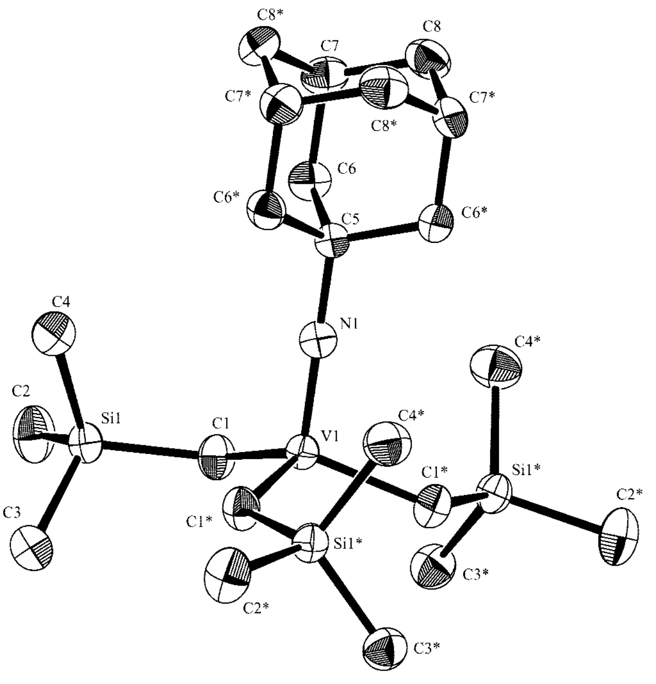
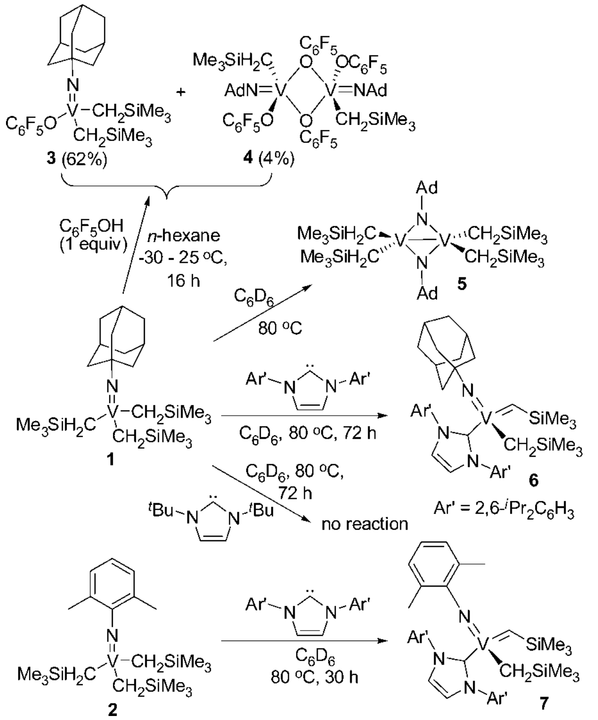


Figure 1. ORTEP drawing for **1**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[10] Selected bond angles (deg) and distances (Å): V−N−C(5) 180.00(17), C(1)−V−C(1)* 112.55(7); V−N 1.6317(14), V(1)−C(1) 2.0267(18).

Scheme 1



the same [112.55(7)°, 2.0267(18) Å], and the facts are also a unique contrast to those in the arylimido-tribenzyl complex.[12]

Reaction of **1** with 1 equiv of C_6F_5OH in *n*-hexane afforded a mixture of $V(NAd)(CH_2SiMe_3)_2(OC_6F_5)$ (**3**, 62% yield) and $[V(NAd)(CH_2SiMe_3)(OC_6F_5)(\mu_2\text{-}OC_6F_5)]_2$ (**4**, 4% yield), as shown in Scheme 1, and these two complexes were isolated by separation and were identified on the basis of NMR spectra and elemental analysis;[10] the structure for **4** could be determined by X-ray crystallography as a dimeric structure bridged by oxygen.[10,13] Although **1** is a low-coordinate unsaturated trialkyl complex, coordination of a donor ligand [such as PMe_3 (14 equiv) and CH_3CN (1 equiv)] was not observed in the ^{51}V NMR spectra (in C_6D_6) at room temperature, as seen in the arylimido analogue (**2**),[6d] probably due to the steric bulk of the three CH_2SiMe_3 ligands. One of the methods commonly employed generating metal−alkylidene is the α-hydrogen abstraction promoted by heat or upon irradiation,[1] but thermolysis of **1** in C_6D_6 at 80 °C afforded a dimeric species, $[V(\mu_2\text{-}NAd)(CH_2SiMe_3)_2]_2$ (**5**), identified by NMR spectra and elemental analysis. The structure of **5** was also confirmed by X-ray crystallography,[14] which was analogous to $[V(\mu_2\text{-}4\text{-}MeC_6H_4)(2,4,6\text{-}Me_3C_6H_2)_2]_2$ reported previously.[15]

N-Heterocyclic carbenes (NHC) have been known to play an essential role as ligands in metal complex catalysts as well as organocatalysts,[16] and NHC in $VOCl_3(IMes)$ [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] previously proposed its utility to stabilize high-oxidation-state vanadium(V) complexes.[17] We thus explored the reaction of **1** in the presence of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (NHC). Coordination of NHC was not seen if **1** was added with 1.0 equiv of NHC in C_6D_6 at 25 °C, but a new resonance ascribed to the alkylidene proton appeared in the ^1H NMR spectrum (13.4 ppm) when the solution was heated at 80 °C for 18 h.[10] Only one resonance in addition to **1** was observed in the ^{51}V NMR spectrum.[10] However, isolation of the targeted complex failed due to the difficulty in separating the product from the NHC remaining in the mixture. Eventually, the targeted complex could be isolated (22% based on NHC, 15% based on V) when **1** was treated with 2/3 equiv of NHC at 80 °C in C_6D_6.[10] The complex could be identified on the basis of NMR spectra and elemental analysis as $V(CHSiMe_3)(NAd)(CH_2SiMe_3)(NHC)$ (**6**), having alkyl, alkylidene, and N-heterocyclic carbene ligands, and the structure could be determined by X-ray crystallography (Figure 2). Similarly, the reaction of the arlyimido analogue (**2**) with NHC afforded $V(CHSiMe_3)(NAr)(CH_2SiMe_3)(NHC)$ (**7**) in better yield (75% based on NHC, 60% based on V) than the adamantylimido analogue (**6**), and **7** was identified on the basis of NMR spectra and elemental analysis. The alkylidene protons ($V{=}CHSiMe_3$) in **6** and **7** were observed at 13.4 ppm as a broad resonance coupled with vanadium, and the resonance is somewhat close to that in $V(CHSiMe_3)(NAr)(N{=}C^tBu_2)(PMe_3)$ (14.52 ppm)[6b] but shifted to low field compared to $V(CHSiMe_3)(NAr)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)$ (16.09 ppm).[6d] However, the

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[13] The reaction of **1** with 1 equiv of $2,6\text{-}Me_2C_6H_3SH$ in *n*-hexane did not take place, as seen in the attempted reaction of **2**.[6d] The reaction of **1** with 1 equiv of $(CF_3)_2CHOH$ in *n*-hexane at 25 °C recovered **1** in high yield even if the mixture was stirred overnight (>12 h),[10] and the results would be an interesting contrast to the fact that the reaction of **2** with $(CF_3)_2C(Me)OH$ cleanly afforded the corresponding alkoxide.[6d] Detailed results are shown in the Supporting Information.

[14] We attempted the crystallographic analysis several times, and the structure could be solved, but the *R* value may not be satisfactory; these results are shown in the Supporting Information.

[15] Synthesis and structural analysis for $[V(\mu_2\text{-}4\text{-}MeC_6H_4)(2,4,6\text{-}Me_3C_6H_2)_2]_2$. Solan, G. A.; Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 2572.

[16] For example: (a) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (b) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Springer: Berlin, Germany, 2007. (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5605.

[17] Abernethy, C. D.; Codd, G. M.; Spicer, M. D.; Taylor, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 1128.

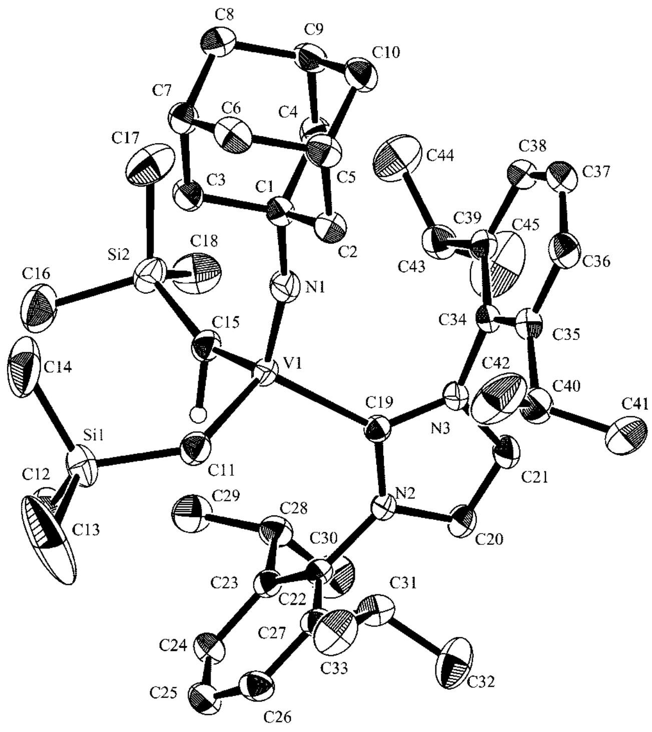

Figure 2. ORTEP drawing for **6**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[10] Selected bond angles (deg) and distances (Å): N−V−C(11) 107.00(12), C(11)−V−C(15) 111.10(12), C(11)−V−C(19) 115.26(11), C(15)−V−C(19) 101.96(11); V−N(1) 1.637(2), V−C(11) 2.069(3), V−C(15) 1.829(3), V−C(19) 2.172(2).

reaction of **1** with (more bulky and stable[18]) 1,3-di-*tert*-butylimidazole-2-ylidene did not show any changes in the ^{51}V NMR spectra even at 80 °C for 3 days (Scheme 1).[10] This thus suggests that this NHC stabilizes **1** probably by weak coordination but did not promote α-hydrogen elimination under these conditions.[19]

The (adamantylimido)vanadium(V)−alkyl, alkylidene complex containing NHC (**6**) has a rather distorted tetrahedral geometry around vanadium (Figure 2), and the V−C bond distances for the alkyl, the alkylidene, and the NHC are 2.069(3), 1.829(3), and 2.172(2) Å, respectively; these values (alkyl, alkylidene) are similar to those in previous reports.[6b,10,17] The V−C(NHC) distance is close to that in VOCl$_3$(IMes) (2.137 Å); the coordination seems like that of neutral carbene, and a similar explanation would be thus possible. Ring-opening metathesis polymerization of norbornene by **6** (and **7**) took place,[20] but the activities (at 80 °C in benzene) were lower than that by V(CHSiMe$_3$)(NAr)(N=C^{t}Bu$_2$)(PMe$_3$)[6b] and the activities at 25 °C were negligible.

We have presented the utility of NHC for stabilization of high-oxidation-state vanadium−alkylidenes (**6** and **7**), and an appropriate donor ligand is necessary to promote α-hydrogen elimination from two adjacent alkyl species. The present approaches should be widely applied for preparation of various early transition metal−alkylidene complexes. Moreover, the present alkyl−alkylidenes would also be promising intermediates for the syntheses of not only alkylidynes but also cationic alkylidenes or alkylidenes containing a series of anionic donor ligands. Further studies concerning their application as catalysts including the effect of adamantyl imido ligands are now under way.

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Supporting Information Available: Text giving experimental procedures, CIF files and structure reports for V(NAd)(CH$_2$SiMe$_3$)$_3$ (**1**), [V(NAd)(CH$_2$SiMe$_3$)(OC$_6$F$_5$)(μ_2-OC$_6$F$_5$)]$_2$ (**4**), [V(μ_2-NAd)(CH$_2$SiMe$_3$)$_2$]$_2$ (**5**), and V(NAd)(CHSiMe)(CH$_2$SiMe$_3$)(NHC) [**6**, NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], and their reactions (described in the text and notes). These materials are available free of charge via the Internet at http://pubs.acs.org.

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[18] Poater, P.; Ragone, F.; Giudice, S.; Costabile, C.; Dorta, R.; Nolan, S. P.; Cavallo, L. *Organometallics* **2008**, *27*, 2679.

[19] Two new resonances (may be ascribed to the alkylidene) were seen in the ^{51}V (and ^{1}H) NMR spectrum when **1** was treated with 14 equiv of PMe$_3$ in C$_6$D$_6$ at 80 °C,[10] but attempted isolation of any complexes from the mixture was unsuccessful.

[20] Conditions: **6** 1.0 μmol, norbornene 200 mg, toluene 5.0 mL, 80 °C for 30 min. Activity 740 turnovers (TON), $M_w = 3.74 \times 10^5$, $M_w/M_n = 2.0$. TON after 1 h was 390 if the reaction with **7** was conducted under the same conditions.