chemistry proceedings

MDPI

Proceeding Paper

A New Method of Alkylarenes Oxidation with MeOH and CCl_4 under the Action of $Mn(acac)_3$ and $Mo(CO)_6$ †

Nina A. Shchadneva [1,*], Alfiya R. Bayguzina [1,2] and Ilfir R. Ramazanov [1,2]

[1] Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa 450075, Russia
[2] Ufa State Petroleum Technological University, 1, Kosmonavtov Str., Ufa 450062, Russia
* Correspondence: Shadneva50@mail.ru; Tel.: +7-905-358-1120

† Presented at the 25th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2021; Available online: https://ecsoc-25.sciforum.net/.

Abstract: Activation of the C–C and C–H bonds are one of the important directions in organic synthesis. Currently, liquid-phase catalytic oxidation of aromatic hydrocarbons has become an independent branch of the technology of organic synthesis. We have developed for the first time a new catalytic method for the preparation of aromatic aldehydes and methyl esters of aromatic carboxylic acids based on the reaction of alkylarenes with methyl hypochlorite generated in situ from the MeOH–CCl_4 reagents under the action of a $Mn(acac)_3$ or $Mo(CO)_6$ catalyst. The optimal molar ratios of catalyst and reagents as well as the reaction conditions for the selective synthesis of aldehydes and methyl esters from alkylaryls were found. In contrast to the known processes of oxidation of aromatic hydrocarbons, the developed method does not require the use of expensive organometallic compounds and molecular oxygen.

Keywords: benzaldehyde; esters; manganesum-catalyzed; methyl hypochlorite; molybdenum-catalyzed; oxidation

Citation: Shchadneva, N.A.; Bayguzina, A.R.; Ramazanov, I.R. A New Method of Alkylarenes Oxidation with MeOH and CCl_4 under the Action of $Mn(acac)_3$ and $Mo(CO)_6$. *Chem. Proc.* **2021**, *3*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Julio A. Seijas

Published: 15 November 2021

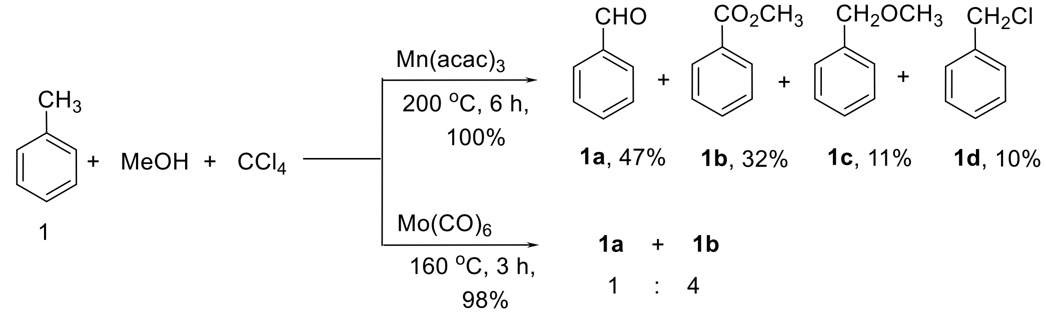
1. Introduction

Activation of the C–C and C–H bonds are one of the important directions in organic synthesis. Currently, liquid-phase catalytic oxidation of aromatic hydrocarbons has become an independent branch of the technology of organic synthesis, which provides raw materials for the production of various polymeric materials (including aromatic resins, fibers and varnishes), pharmaceutical and perfumery preparations, agricultural chemicals, dyes, solvents and special chemicals [1].

Toluene, the simplest and most readily available alkylarene, was catalytically converted to oxidized products such as benzyl alcohol, benzyl alkyl ether, benzaldehyde, and aromatic carboxylates [2,3]. There are methods for the preparation of aromatic carboxylates by oxidative esterification of methylarenes with alcohols using homogeneous organophotocatalysis (CBr_4 or anthraquinone-2,3-dicarboxylic acid) under irradiation with light [4,5], as well as direct esterification of alkylaryls with alcohols, catalyzed by Bu_4NI and *tert*-butyl hydroperoxide as an oxidizing agent [6], nanoparticles of bimetallic Au-Pd catalyst, $Co(OAc)_2$–*N*-hydroxyphthalimide with the addition of an ionic liquid or hexafluoropropan-2-ol, CuI–1,10-phen and molecular oxygen as an oxidizing agent [7–10]. Oxidation of toluene with iron perchlorate $Fe(OCl_4)_2$ with H_2O_2–H_2O–CH_3CN system proceeds with the formation of benzyl alcohol and benzaldehyde [11]. However, all these methods have not received wide synthetic application due to the use of expensive catalysts and stoichiometric amounts of oxidants and molecular oxygen. We were the first to develop a new catalytic method for the preparation of aromatic aldehydes and methyl esters of aromatic carboxylic acids, based on the reaction of alkylaryls with methyl hypochlorite generated in situ from MeOH–CCl_4 reagent system under the action of the Mn(acac)$_3$ or Mo(CO)$_6$ catalyst, excluding the use of both expensive organometallic compounds and molecular oxygen.

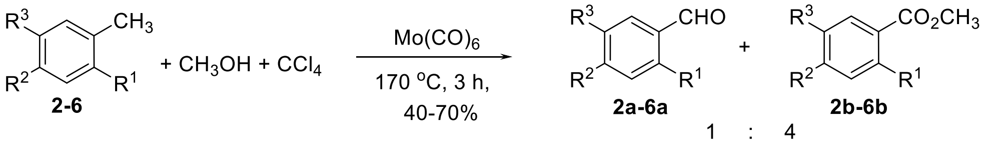
2. Results and Discussion

We found that the reaction of toluene **1** with MeOH–CCl_4–Mn(acac)$_3$reagent system ([Mn(acac)$_3$]:[CCl_4]:[MeOH]:[toluene] = 1:300:500:100–150 at 200 °C for 6 h gives benzaldehyde **1a** (47%), methyl benzoate **1b** (32%), benzyl methyl ether **1c** (11%) and benzyl chloride **1d** (10%) (Scheme 1). Besides MeOH–CCl_4reagent system rather actively oxidizes toluene in the presence of Mo(CO)$_6$ at 160 °C for 3 hours. Inthis case the main reaction products were benzaldehyde **1a** and methyl benzoate **1b** in a ratio of 1: 4, respectively.We suggest that the observed process is based on the reaction of alkylaryls with methyl hypochlorite generated in situ from the MeOH–CCl_4 reagent system under the action of Mn(acac)$_3$or Mo(CO)$_6$ catalysts.



Scheme 1. Mn- and Mo-catalyzed oxidation of toluene by MeOH–CCl_4 reagent system.

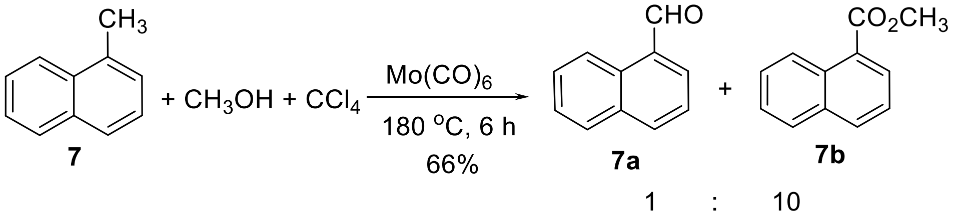
It was found that Mo-catalyzed oxidation of di-, tri- and tetramethylbenzenes by MeOH–CCl_4 reagent system proceeds selectively at one methyl group, while the remaining methyl groups remain unreacted (Scheme 2).



2a, 2b: R^1 = CH_3, R^2 = R^3 = H (39%); 3a,b: R^1 = R^3 = H, R^2 = CH_3 (70%); 4a,b: R^1 = R^2 = H, R^3 = CH_3 (58%);
5a,b: R^1 = R^2 = CH_3, R^3 = H (70%); **6a,b:** R^1 = R^2 = R^3 = CH_3 (49%)

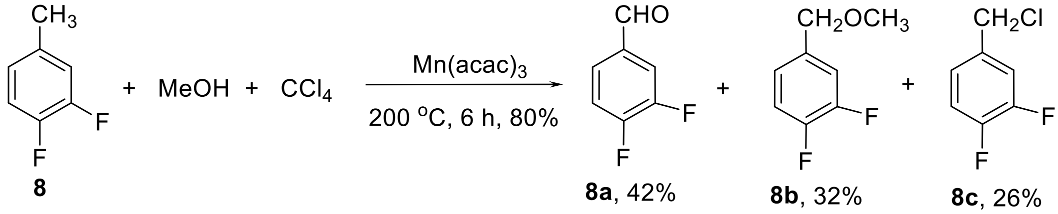
Scheme 2. Mo-catalyzed oxidation of di-, tri- and tetramethylbenzenes by MeOH–CCl_4 reagent system.

1-Methylnaphthalene **7**was oxidized with MeOH–CCl_4–Mo(CO)$_6$reagent system at 180 °C for 6 hours with the formation of naphthylaldehyde **7a** and methyl ester of 1-naphthoic acid **7b** at a ratio of 1:10, respectively (Scheme 3).



Scheme 3. Mo-Catalyzed oxidation of 1-methylnaphthalene by MeOH–CCl_4 reagent system.

Oxidation of methylarenes with additional polar substituents in the aromatic ring proceeds with difficulty and low selectivity. For example, the oxidation of 3,4-difluorotoluene 8 with the MeOH–CCl_4–Mn(acac)$_3$reagent systemstops at the stage of obtaining 3,4-difluorobenzaldehyde **8a** (Scheme 4).



Scheme 4. Mn-catalyzed oxidation of 3,4-difluorotoluene by MeOH–CCl_4 reagent system.

3. Conclusions

A new catalytic method for the preparation of aromatic aldehydes and methyl esters of aromatic carboxylic acids based on the reaction of alkylaryls with methyl hypochlorite generated in situ from the MeOH–CCl_4 reagents under the action of Mn(acac)$_3$ or Mo(CO)$_6$ catalysts has been developed. The optimal molar ratios of catalyst and reagents as well as the reaction conditions for the selective synthesis of aldehydes and methyl esters from alkylaryls have been found.

4. Experimental Part

Commercially available reagents were used. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer (100.62 MHz for ^{13}C and 400.13 MHz for ^{1}H). When recording the ^{1}H and ^{13}C NMR spectra, $SiMe_4$ and $CDCl_3$ were used as an internal standards, respectively. Mass spectra were measured using Finnigan 4021 instrument with an ionizing electron energy of 70 eV and an ionization chamber temperature of 200 ° C. The elemental analysis of the samples was determined on Carlo Erba elemental analyzer, model 1106.

The Procedure for Oxidation of Alkylaranes

The reactions were carried out in glass ampoule (V = 10 mL) placed in a stainless microautoclave (V = 17 mL) with continuous stirring and controlled heating. An ampoule was charged under argon with 0.05 mmol of Mn(acac)$_3$ (or Mo(CO)$_6$), 0.1 mmol alkylarene, 1–3 mmol CCl_4 and 1–3 mmol methanol. The sealed ampoule was heated in the autoclave at 160–200 °C for 3–6 h with vigorous stirring. After there action completion, the autoclave was cooled to 20 °C, the reaction mixture was neutralized with a 10% Na_2CO_3 aqueous solution, the organic layer was extracted with chloroform, and the extract was filtered through a layer of alumina. The unreacted toluene, light ethers, and chloroform were removed on a rotor evaporator. The residue was analyzed by GLC using decane as an internal standard.

Author Contributions: Conceptualization, N.A.S.; methodology, N.A.S.; software, I.R.R.; validation, A.R.B.; formal analysis, A.R.B.; investigation, N.A.S.; resources, I.R.R.; data curation, A.R.B.; writing—original draft preparation, A.R.B.; writing—review and editing, I.R.R.; visualization, A.R.B.; supervision, N.A.S.; project administration, N.A.S.; funding acquisition, I.R.R.

Funding: The work was carried out within the framework of the state assignment of the Ministry of Education and Science (No. AAAA-A19-119022290009-3 and No. AAAA-A19-119022290008-6).

Acknowledgments: The authors thank the Shared Facility Center «Agidel», Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, for the registration of NMR and mass spectra and for the elemental analysis of new compounds.

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

References

1. Vanjari, R.; Singh, K.N. Utilization of methylarenes as versatile building blocks in organic synthesis. *Chem. Soc. Rev.* **2015**, *44*, 8062–8096. https://doi.org/10.1039/c5cs00003c.
2. Khusnutdinov, R.I.; Bayaguzina, A.R.; Dzhemilev, U.M. Advances in the Synthesis of Aromatic and Heteroaromatic Carboxylic Acids and Their Esters. *Russ. J. Org. Chem.* **2017**, *53*, 1113–1169. https://doi.org/10.1134/S1070428017080012.
3. Sterckx, H.; Morel, B.; Maes, B.U.W. Recent advances in catalytic aerobic oxidation of C(sp^3)–H bonds. *Angew. Chem. Int. Ed.* **2019**, *58*, 7946–7970. http://dx.doi.org/10.1002/anie.201804946.
4. Nobuta, T.; Fujiya, A.; Hirashima, S.-i.; Tada, N.; Miura, T.; Itoh, A. Aerobic oxidative esterification of benzyl alcohols with catalytic tetrabromomethane under visible light irradiation. *Tetrahedron Lett.,* **2012**, *53*, 5306–5308. http://dx.doi.org/10.1016/j.tetlet.2012.07.091.
5. Tada, N.; Ikebata, Y.; Nobuta, T.; Hirashima, S.; Miura, T.; Itoh, A. Direct aerobic photo-oxidative syntheses of aromatic methyl esters from methyl aromatics using anthraquinone-2,3-dicarboxylic acid as organophotocatalyst. *Photochem. Photobiol. Sci.* **2012**, *11*, 616–619. https://doi.org/10.1039/c2pp05387j.
6. Liu, L.; Yun, L.; Wang, Z.; Fu, X.; Yan, C.-h.Transition metal free oxidative esterification of alcohols with toluene. *Tetrahedron Lett.* **2013**, *54*, 5383–5386. http://dx.doi.org/10.1016/j.tetlet.2013.07.11.
7. Liu, H.; Chen, G.; Jiang, H.; Li, Y.; Luque, R. From Alkyl Aromatics to Aromatic Esters: Efficient and Selective C–HActivation Promoted by a Bimetallic Heterogeneous Catalyst. *ChemSusChem.* **2012**, *5*, 1892–1896. http://dx.doi.org/10.1002/cssc.201200611.
8. Mahmood, S.; Xu, B.-H.; Ren, T.-L.; Zhang, Z.-B.; X.-M.; Zhang, S.-J. Cobalt/*N*-Hydroxyphthalimide (NHPI)-Catalyzed Aerobic Oxidation of Hydrocarbons with Ionic Liquid Additive. *Mol. Catal.* **2018**, *447*, 90–96. https://doi.org/10.1016/j.mcat.2018.01.006.
9. Gaster, E.;Kozuch, S.;Pappo, D. Selective Aerobic Oxidation of Methylarenestobenzaldehydes Catalyzed by *N*-Hydroxy-phthalimide and Cobalt (II) Acetate in Hexafluoropropa-2-ol. *Angew. Chem. Int. Ed.* **2017**, *56*, 5912–5915. https://doi.org/10.1002/anie.201702511.
10. Liu, M.; Chen, T.; Yin, S.-F. Copper-Catalysed Aerobic Oxidative Esterification on *N*-HeteroarylMethanes with Alcohols. *Catal. Sci. Technol.* **2016**, *6*, 690–693. https://doi.org/10.1039/C5CY02069G.
11. Ramu, R.; Wanna, W.H.; Janmanchi, D.; Tsai, Y.-F.; Liu, C.-C.; Mou, C.-Y.; Yu, S.S.-F. Mechanistic study for the selective oxidation of benzene and toluene catalyzed by Fe(ClO$_4$)$_2$ in an H$_2$O$_2$–H$_2$O–CH$_3$CN systems. *Mol. Catal.* **2017**, *441*, 114–121. http://dx.doi.org/10.1016/j.mcat.2017.08.006.