Asian Pub. Corp.

www.asianpubs.org

ARTICLE

Selective Oxidation of Benzyl Halides to Benzaldehydes by Phase Transfer Catalyzed Monochromate Ions in Non-Polar Solvents

K. Bijudas✉ and P. Bashpa

ABSTRACT

Benzyl chloride, benzyl bromide and their *para* substituted derivatives were selectively oxidized to corresponding benzaldehydes by acidified monochromate in toluene and ethyl acetate with the help of phase transfer catalysts like tetrabutylphosphonium bromide (TBPB), tetrabutylammonium bromide (TBAB), tetrabutylammonium hydrogen sulphate (TBAHS), cetyltrimethylammonium bromide (CTMAB) and tricaprylmethylammonium chloride (TCMC). The reaction was carried out by simple magnetic stirring for about 2 h at 60 ºC. The products were recrystallized and analyzed by infrared and UV-visible spectral techniques. Benzaldehyde and substituted benzaldehydes were formed in good yield (> 90%) on oxidation of benzyl chlorides and benzyl bromides. The reaction is proved to be highly selective due to the absence of acids or any other products during the reaction. All the phase transfer catalysts were highly effective in bringing out the reaction in both the solvents. This is highly significant as the oxidation reaction will not occur in non-polar solvents without the presence of phase transfer catalysts.

Asian Journal of Organic & Medicinal Chemistry

Volume: 5 Year: 2020
Issue: 3 Month: July–September
pp: 249–253
DOI: https://doi.org/10.14233/ajomc.2020.AJOMC-P287

Received: 4 May 2020
Accepted: 10 September 2020
Published: 15 September 2020

KEYWORDS

Benzyl chloride, Benzyl bromide, Selective oxidation, Monochromate ion, Phase transfer catalysis.

Author affiliations:

Department of Chemistry, N.S.S. College, Manjeri, Malappuram, Kerala-676122, India

✉To whom correspondence to be addressed:

Fax: +91 483 2766975
E-mail: bijudask@gmail.com

INTRODUCTION

Oxidation is an important type of reaction for manufacturing of various chemicals of industrial significance. Usually, oxidizing agents like permanganate, dichromate, hypochlorite, hydrogen peroxide, bromate, ferrate *etc*. are used for the oxidation of organic compounds [1-5]. But these reactions are very slow even at high temperature due to the inability of inorganic oxidants to dissolve in organic solvents where the substrate is dissolved. Rapid stirring at high temperature and the use of dipolar aprotic solvents like dimethyl sulphoxide (DMSO) or dimethylformamide (DMF) were the earlier methods to conduct such reactions [6-8]. The application of dipolar aprotic solvents had brought some improvements in such reactions. But disadvantages like the toxicity and high cost of DMSO and DMF, requirement of high reaction time and temperature, difficulty in product separation, lack of purity of products, *etc*. adversely affected this method for a wider application.

Phase transfer catalysis (PTC) can easily overcome these problems in such situations. This technique has been shown to enhance the reactivity in different types of reactions. The method involves transfer of inorganic anions from the polar medium into the non-polar organic medium in the form of an ion-pair with the cationic moiety of the phase transfer catalyst with appropriate size and lipophilicity. The anions thus transferred and poorly solvated in the organic media exhibit greater reactivity. This enables the substrate to react faster in the non-polar media in the presence of phase transfer catalyst. Phase transfer catalysis is a powerful tool used in various chemical industries [9-11]. The reaction can be accomplished in a biphasic system involving an inexpensive non-polar aprotic solvent and water without using DMSO or DMF which are highly polar solvents. A phase transfer catalyst is soluble in both solvents and hence can carry anions of inorganic salts into organic solvents as an ion pair and returns them into the water phase after the reaction is over. Reactions usually progress smoothly under mild conditions with easy workup procedures. The scope of PTC technology is most appropriately understood by considering a range of reactions for which PTC is made applicable [12,13]. Typical phase-transfer catalysts are quaternary ammonium salts, crown ethers and phosphonium compounds, *etc*. [14-16]. Other compounds like *n*-alkyl phosphoramides (particularly *n*-dodecyl or *n*-hexadecyl), methylene bridged phosphorous and sulphur oxides, *tris*[2-(2-methoxyethoxy)ethyl]amine (TDA-1) are also used as phase transfer catalysts. Sufficient reports are available on the selective oxidation of primary and secondary alcohols to aldehydes by chromate, hypochlorite, permanganate, *etc*. in non-polar medium under PTC [17-22]. But such reports on the selective oxidation of benzyl halides are scanty and hence the present work is reported [23-25].

The present paper reports the selective oxidation of benzyl chloride, benzyl bromide and their *para* substituted derivatives by acidified monochromate with the aid of various quaternary ammonium and phosphonium salts as phase transfer catalysts in ethyl acetate and toluene by stirring using a magnetic stirrer at 60 °C for about 2 h.

EXPERIMENTAL

Potassium dichromate and sodium carbonate (extra pure, AR, Sisco Research Laboratories Pvt. Ltd., India) were used as such throughout the experiment and their solutions were prepared in doubly distilled water. Benzyl chloride and benzyl bromide (Spectrochem Pvt. Ltd., India) was distilled under reduced pressure for further purification. 4-Chlorobenzyl bromide, 4-bromobenzyl chloride, 4-nitrobenzyl chloride, 4-methoxybenzyl chloride, 4-methoxybenzyl bromide, 4-methylbenzyl chloride, 4-methylbenzyl bromide, 4-hydroxybenzyl chloride, 4-hydroxybenzyl bromide (Sigma-Aldrich Chemicals Pvt. Ltd., India), 4-bromobenzyl bromide, 4-chlorobenzyl chloride and 4-nitrobenzyl bromide (Spectrochem Pvt. Ltd., India) were of high purity. The phase transfer catalysts, tetrabutylammonium bromide (TBPB) (Merck KGaA, Germany), tetrabutylammonium bromide (TBAB), cetyltrimethylammonium bromide (CTMAB), tetrabutylammonium hydrogen sulphate (TBAHS) and tricaprylmethylammonium chloride (TCMAC) (Sisco Research Laboratories Pvt. Ltd., India) were also used as such. The organic solvents, toluene and ethyl acetate (Sisco Research Laboratories Pvt. Ltd., India) were used after purification according to the standard procedure [26,27].

General procedure: The stoichiometry of the reaction between benzyl halide and acidified monochromate ions was determined by taking excess of [monochromate] over [benzyl halide] and allowing the reaction for completion at 60 °C. Under this condition, all the benzyl halides taken would be completely reacted leaving the unreacted monochromate. The concentration of remaining monochromate was estimated spectrophotometrically at 365 nm and from this, the stoichiometry of the reaction is determined.

Oxidation of benzyl halides were carried out in a heterogeneous fashion. Benzyl chloride and benzyl bromide (0.1 mol) were dissolved in 50 mL ethyl acetate and toluene containing 0.01 mol phase transfer catalyst and were mixed with 50 mL $K_2Cr_2O_7$ (0.5 mol) containing 2 mol dm^{-3} H_2SO_4 and a pinch of sodium carbonate. These reaction mixtures were stirred vigorously using a magnetic stirrer for about 2 h at 60 °C. The organic layers of the reaction mixtures were extracted with ether three times after the completion of the reaction. These organic layers were again extracted with 10% sodium bicarbonate solution and both organic and aqueous layers were separated. A saturated solution of 2,4-dinitrophenylhydrazine in HCl was added to the organic layers and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) of both the oxidation reactions were filtered off, dried and weighed. The products after recrystallization from ethanol were characterized by its melting point in triplicate and other qualitative analytical techniques like infrared and UV-visible spectroscopy. The aqueous layers after extraction with sodium bicarbonate were acidified with conc. HCl. This procedure was repeated with substituted benzyl chlorides and benzyl bromides in ethyl acetate and toluene using various phase transfer catalysts.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was established by equilibrating known excess concentration of the phase transferred monochromate with known amount of the benzyl halide. One mole of monochromate was found to be equivalent to three moles of benzyl halides.

$$3PhCH_2X + Cr(VI) \longrightarrow 3PhCHO + Cr(IV) + 6HX$$

$$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III)$$

where X = Cl or Br

The products on oxidation of benzyl halides by acidified monochromate in non-polar solvents were precipitated in the form of DNP and have been recrystallized from ethanol. The recrystallized products after drying were characterized by its melting point in triplicate. The melting points of 2,4-dinitrophenylhydrazone (DNP) of products of benzyl chlorides and bromides are given in Table-1.

The infrared absorption spectra of the products by taking benzyl chloride and benzyl bromide as standards on oxidation by acidified monochromate were recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan). The infrared spectral data of products formed on the monochromate oxidation of benzyl halides and substituted benzyl halides are given below:

TABLE-1
MELTING POINTS OF PRODUCTS ON OXIDATION OF BENZYL HALIDES AND SUBSTITUTED BENZYL HALIDES BY MONOCHROMATE

Substrate	Melting point (°C)	
	Chloride	Bromide
Benzyl halide	235 ± 2	234 ± 2
4-Chlorobenzyl halide	252 ± 2	254 ± 2
4-Bromobenzyl halide	257 ± 2	255 ± 2
4-Hydroxybenzyl halide	272 ± 2	270 ± 2
4-Methoxybenzyl halide	251 ± 2	250 ± 2
4-Methylbenzyl halide	230 ± 2	232 ± 2
4-Nitrobenzyl halide	320 ± 2	321 ± 2

Halide = chloride or bromide

2,4-Dinitrophenyl hydrazone of benzaldehyde: Yield 92%; orange solid; m.p.: 235 °C, m.w.: 286.24; IR (KBr, ν_{max}, cm^{-1}): 3290 (N–H), 3090 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH). UV-visible (ethanol, λ_{max}, nm): 235 (π-π^*), 355 (n-π^*).

2,4-Dinitrophenyl hydrazone of 4-chlorobenzaldehyde: Yield 89%; orange solid; m.p.: 252 ºC, m.w.: 320.69; IR (KBr, ν_{max}, cm^{-1}): 3285 (N–H), 3080 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH), 860 (C-Cl).

2,4-Dinitrophenyl hydrazone of 4-bromobenzaldehyde: Yield 88%; orange solid; m.p.: 257 °C, m.w.: 445.04; IR (KBr, ν_{max}, cm^{-1}): 3285 (N–H), 3080 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH), 670 (C-Br).

2,4-Dinitrophenyl hydrazone of 4-hydroxybenzaldehyde: Yield 91%; orange solid; m.p.: 272 °C, m.w.: 302.24; IR (KBr, ν_{max}, cm^{-1}): 3290 (N–H), 3090 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH), 3620 (O-H).

2,4-Dinitrophenyl hydrazone of 4-methoxybenzaldehyde: Yield 93%; orange solid; m.p.: 251 °C, m.w.: 316.27; IR (KBr, ν_{max}, cm^{-1}): 3295 (N–H), 3110 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH), 2790 (C-H).

2,4-Dinitrophenyl hydrazone of 4-methylbenzaldehyde: Yield 92%; orange solid; m.p.: 230 °C, m.w.: 300.27; IR (KBr, ν_{max}, cm^{-1}): 3295 (N–H), 3110 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH), 2875 (C-H).

2,4-Dinitrophenyl hydrazone of 4-nitrobenzaldehyde: Yield 87%; orange solid; m.p.: 320 °C, m.w.: 331.27; IR (KBr, ν_{max}, cm^{-1}): 3290 (N–H), 3080 (C–H), 1750 (C=N), 1630 (C=C), 1510 (Ar–NO_2 asymm), 1330 (Ar–NO_2 sym), 1140 (C-NH), 1540 (Ar-NO_2)

All the infrared spectra of products on oxidation with acidified monochromate were compared with that of available in literature and ascertained the formation of benzaldehyde and *para* substituted benzaldehydes as products on oxidation of corresponding benzyl halides.

The UV-visible absorption spectra of the products by taking benzyl chloride and benzyl bromide as standards on oxidation by acidified monochromate were recorded by Hitachi U-3000 UV-visible spectrophotometer using 1 cm quartz cell and spectro grade ethanol (Merck, India) as solvent which is given in Fig. 1. The UV-visible spectrum of DNP of product on the oxidation of benzyl chloride showed intense peaks at 235 and 355 nm and were assigned to π-π^* and n-π^* transitions of the compound which are characteristics of DNP of benzaldehyde. The product absorbs UV radiation due to transition of electrons from highest occupied molecular orbital (HOMO) to highest unoccupied molecular orbital (LUMO).

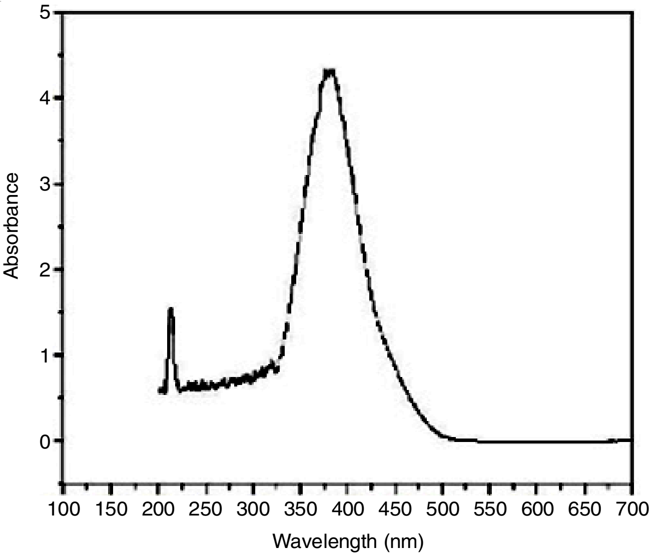

Fig. 1. UV-visible spectrum of DNP of product on oxidation of benzyl chloride

Oxidation of benzyl chlorides and benzyl bromides by acidified monochromate ions in non-polar solvents under phase transfer catalysis gave corresponding benzaldehydes. This procedure is found to be highly selective since there is no traces of acids and benzaldehyde and substituted benzaldehydes were formed with high yield and purity. All the phase transfer catalysts performed well in their catalytic activity in oxidation reactions but the yield and ease of reaction is slightly different and is in the order TCMAC > TBPB > TBAB > TBAHS > CTMAB. This is due to changes in combination of alkyl or aryl groups and also may be due to the difference in the activity of anions for phase transfer as explained earlier [11]. The primary requirement of the cationic part of phase transfer catalyst is that they collectively should have sufficient organic structure to transfer the desired anion into the organic phase. It is already established that larger alkyl or aryl groups with almost symmetric structure are most effective both in anion transfer and in reactivity. Therefore, TCMAC with more bulky and symmetrical alkyl groups has higher reactivity on comparison with other phase transfer catalyst used. Even though both TBPB and TBAB have same alkyl moiety, phosphonium is always a better central onium atom with more reactivity than ammonium and So TBPB gives higher yield of the product than TBAB. Both TBAHS and CTMAB are also considered as good phase transfer catalysts but there is a tendency to form an emulsion in most of the reactions involving these catalysts. The reaction took place with ease in both ethyl acetate and toluene but yield of product is found to be slightly more in ethyl acetate than that in toluene. The solubility and partitioning behaviour of the quaternary salts are markedly affected by slight changes in the nature of organic phase. Solubility and partitioning of quaternary salts are increased by increasing the polarity of the aprotic organic phase. Ethyl acetate is more polar than toluene and therefore the former is a better solvent than toluene in terms of ease of reaction, better yield and on consideration as a green solvent. Based on the experimental results obtained, a possible Stark's phase transfer catalytic cycle is given in **Scheme-I** for benzyl chlorides and in **Scheme-II** for benzyl bromides.

$$\begin{tikzcd}
Q^+HCrO_4^- + PhCH_2Cl \arrow[r, harpoon, shift left] \arrow[d, harpoon, shift left] & PhCHO + Q^+X^- \arrow[l, harpoon, shift left] \arrow[d, harpoon, shift left] \\
Q^+HCrO_4^- + K^+X^- \arrow[u, harpoon, shift left] \arrow[r, harpoon, shift left] & K^+HCrO_4^- + Q^+X^- \arrow[l, harpoon, shift left] \arrow[u, harpoon, shift left]
\end{tikzcd}$$

Scheme-I: Stark's catalytic cycle for the oxidation of benzyl chloride

$$\begin{tikzcd}
Q^+HCrO_4^- + PhCH_2Br \arrow[r, harpoon, shift left] \arrow[d, harpoon, shift left] & PhCHO + Q^+X^- \arrow[l, harpoon, shift left] \arrow[d, harpoon, shift left] \\
Q^+HCrO_4^- + K^+X^- \arrow[u, harpoon, shift left] \arrow[r, harpoon, shift left] & K^+HCrO_4^- + Q^+X^- \arrow[l, harpoon, shift left] \arrow[u, harpoon, shift left]
\end{tikzcd}$$

Scheme-II: Stark's catalytic cycle for the oxidation of benzyl bromide

A possible mechanism for the selective oxidation of benzyl halides and *para* substituted benzyl halides by acidified monochromate in non-polar medium can be formulated and explained as follows. The conversion of benzyl halides and *para* substituted benzyl halides to benzaldehydes and corresponding *para* substituted benzaldehydes took place in two stages. In the first stage, benzyl halides were oxidized to corresponding benzyl alcohols by monochromate and subsequently these benzyl alcohols were selectively oxidized to corresponding benzaldehydes. Even though the reaction took place in two stages, there was no formation of any other byproducts during the entire course of the reaction. Monochromate ions were identified as the active oxidant species which is formed in acidified potassium dichromate solution with a pinch of sodium carbonate in order to keep the pH in the range 6-8. These reaction sequences are given in **Scheme-III**.

$$\begin{aligned}
K_2Cr_2O_7 &\rightleftharpoons Cr_2O_7^{2-} + 2K^+ \\
Cr_2O_7^{2-} + H_2O &\rightleftharpoons 2HCrO_4^- \\
Na_2CO_3 + Cr_2O_7^{2-} &\rightleftharpoons 2Na^+ + 2CrO_4^{2-} + CO_2 \\
CrO_4^{2-} + H^+ &\rightleftharpoons HCrO_4^-
\end{aligned}$$

Scheme-III: PTC reactions in aqueous phase

Addition of sodium carbonate helps to keep the pH at 6-8 which promotes the formation of monochromate ions in the aqueous medium. Sodium carbonate reacted with dichromate ions forming chromate ions which on reaction with sulphuric acid forms acidified monochromate ion as the predominant species. The monochromate ion formed in the aqueous phase is transferred to the organic phase as an ion pair and shown in **Scheme-IV**.

$$\begin{aligned}
(Q^+X^-)_{aq} + (HCrO_4^-)_{aq} &\rightleftharpoons (Q^+HCrO_4^-)_{aq} + X^-_{aq} \\
(Q^+HCrO_4^-)_{aq} &\rightleftharpoons (Q^+HCrO_4^-)_{org}
\end{aligned}$$

Scheme-IV: Phase transfer of active oxidant as an ion-pair

The monochromate ions in the form of ion-pair in the organic phase is still reactive and oxidised benzyl halides first to benzyl alcohol and then to benzaldehyde in a selective manner with ease which is given in **Scheme-V**.

$$\begin{aligned}
PhCH_2X + (Q^+HCrO_4^-)_{org} &\rightleftharpoons PhCH_2OCrO_3H + (Q^+X^-)_{org} \\
PhCH_2OCrO_3H &\rightleftharpoons PhCH_2OH + CrO_3 \\
PhCH_2OH + (Q^+HCrO_4^-)_{org} &\rightleftharpoons PhCH_2OCrO_3^-Q^+ + H_2O \\
PhCH_2OCrO_3^-Q^+ &\rightleftharpoons PhCHO + CrO_2 + Q^+ + H^+ \\
HCrO_4^- + H^+ &\rightleftharpoons H_2CrO_4 \\
(Q^+X^-)_{org} &\rightleftharpoons (Q^+X^-)_{aq}
\end{aligned}$$

Scheme-V: Oxidation of benzyl halides by monochromate in organic medium

Benzyl halides interacts with monochromate ions forming a chromate ester which enjoys more stability in organic phase rather than aqueous phase. Chromium(V) and chromium(IV) are the possible intermediates in these reactions. Benzyl alcohol formed *in situ* reacts further with monochromate in the organic phase forming benzaldehyde. The ion-pair, after the reaction returns back to the aqueous phase so as to complete the Stark's cycle. The same reaction sequence is followed by all *para* substituted benzyl halides.

Conclusion

Oxidation of benzyl chlorides and benzyl bromides has been carried out in toluene and ethyl acetate using acidified monochromate as oxidant under phase transfer catalytic (PTC) method. Sodium carbonate is added to the aqueous medium to keep the pH between 6-8 which felicitates the transfer of monochromate ions from the aqueous phase to organic phase as an ion-pair. The phase transferred monochromate first oxidized benzyl halides to benzyl alcohols and in the second stage it effects the oxidation of benzyl alcohols to corresponding benzaldehydes. The products were identified as benzaldehyde and substituted benzaldehydes in a selective manner with excellent yield. The method adopted for oxidation is highly significant in terms of use of greener solvents, lower reaction time and temperature, high yield of products and no byproduct formation.

REFERENCES

1. K.B. Wiberg, Oxidation in Organic Chemistry, Academic Press: London and New York (1965).
2. S. Paterson, Alcohol oxidation: Reaction, Effects and Applications, Nova Science Publishers, Inc., New York (2018).
3. S. Dash, S. Patel and B.K. Mishra, Oxidation by Permanganate: Synthetic and Mechanistic Aspects, *Tetrahedron*, **65**, 707 (2009); https://doi.org/10.1016/j.tet.2008.10.038
4. K. Bijudas, Kinetics and Mechanism of the Selective Oxidation of Benzyl Alcohols by Acidified Dichromate in Aqueous Acetic Acid Medium, *Orient. J. Chem.*, **30**, 1391 (2014); https://doi.org/10.13005/ojc/300360
5. Z. Hu, L. Ma, J. Xie, H. Du, W.W.Y. Lam and T.-C. Lau, Ruthenium-Catalyzed Oxidation of Alcohols by Bromate in Water, *New J. Chem.*, **37**, 1707 (2013); https://doi.org/10.1039/c3nj00102d
6. D. Dey and M.K. Mahanti, Kinetics of Oxidation of Substituted Benzyl Alcohols by Quinolinium Dichromate, *J. Org. Chem.*, **55**, 5848 (1990); https://doi.org/10.1021/jo00310a015

7. P.D. Sharma, P. Panchariya, P. Purohit and P.K. Sharma, Structure-Reactivity Correlation in the Oxidation of Substituted Benzyl Alcohols by Imidazolium Fluorochromate, *Eur. Chem. Bull.*, **2**, 816 (2013); https://doi.org/10.17628/ECB.2013.2.816
8. T. Mallat and A. Baiker, Reactions in "Sacrificial" Solvents, *Catal. Sci. Technol.*, **1**, 1572 (2011); https://doi.org/10.1039/c1cy00207d
9. E.V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis, VCH, Weinheim: Germany (1993).
10. Y. Sasson and R. Neumann, Handbook of Phase Transfer Catalysis, Kluwer Academic Publishers; Dordrecht (1993).
11. C.M. Starks and C.L. Liotta, Phase-Transfer Catalysis, In: Fundamentals I.: Phase Transfer Catalysis, Principles and Techniques, Academic Press, New York (1978).
12. M. Makosza, Phase-Transfer Catalysis. A General Green Methodology in Organic Synthesis, *Pure Appl. Chem.*, **72**, 1399 (2000); https://doi.org/10.1351/pac200072071399
13. G. Ilia, S. Iliescu and A. Popa, Polymer-Supported Phase Transfer Catalysts in Green Organic Syntheses, *Curr. Green Chem.*, **2**, 264 (2015); https://doi.org/10.2174/2213346102999150306112846
14. R.A. Jones, Quaternary Ammonium Salts, Their Use in Phase-Transfer Catalysed Reactions, Academic Press, New York (2001).
15. S.E. Denmark, N.D. Gould, L.M. Wolf, Synthesis of Catalyst Libraries and Evaluation of Catalyst Activity, A Systematic Investigation of Quaternary Ammonium Ions as Asymmetric Phase-Transfer Catalysts. Synthesis of Catalyst Libraries and Evaluation of Catalyst Activity, *J. Org. Chem.*, **76**, 4260 (2011); https://doi.org/10.1021/jo2005445
16. K.V. Ponmuthu, D. Kumaraguru, J.B. Arockiam, S. Velu, M. Sepperumal and S. Ayyanar, New Quaternary Phosphonium Salt as Multi-Site Phase-Transfer Catalyst for Various Alkylation Reactions, *Res. Chem. Intermed.*, **42**, 8345 (2016); https://doi.org/10.1007/s11164-016-2600-1
17. D. Pletcher and S.J.D. Tait, The Oxidation of Alcohols and Aromatic Hydrocarbons by Dichromate in Two Phase Systems, *J. Chem. Soc. Perkin Trans. 2*, 788 (1978); https://doi.org/10.1039/P29790000788
18. K. Bijudas and T.D. Radhakrishnan Nair, Selective Oxidation of Benzyl Alcohol with Monochromate in Non-polar Solvents, *Indian J. Chem.*, **43A**, 1216 (2004).
19. D.C.M. Albanese, F. Foschi and M. Penso, Sustainable Oxidations under Phase-Transfer Catalysis Conditions, *Org. Process Res. Dev.*, **20**, 129 (2016); https://doi.org/10.1021/acs.oprd.5b00385
20. A.C. Ranveer, S.V. Ranade and C.K. Mistry, Selective Oxidation of Lauryl Alcohol to Lauraldehyde under Liquid-Liquid Phase Transfer Catalysis (LL-PTC) with Potassium Chromate as the Oxidizing Agent, *Iran. J. Chem. Chem. Eng.*, **37**, 89 (2018).
21. K. Bijudas, P. Bashpa, V.P. Bipin, L. Nair, A.P. Priya, M. Aswathi, C. Krishnendu and P. Lisha, Selective Synthesis of Benzaldehydes by Hypochlorite Oxidation of Benzyl Alcohols under Phase Transfer Catalysis, *Bull. Chem. React. Eng. Catal.*, **10**, 38 (2015); https://doi.org/10.9767/bcrec.10.1.7189.38-42
22. A.N. Ajjou and A. Rahman, Green Organic Solvent-Free Oxidation of Alkylarenes with *tert*-Butyl Hydroperoxide Catalyzed by Water-Soluble Copper Complex, *Open Chem.*, **18**, 165 (2020); https://doi.org/10.1515/chem-2020-0018
23. G.D. Yadav and B.V. Haldavanekar, Mechanistic and Kinetic Investigation of Liquid-Liquid Phase Transfer Catalyzed Oxidation of Benzyl Chloride to Benzaldehyde, *J. Phys. Chem. A*, **101**, 36 (1997); https://doi.org/10.1021/jp961678x
24. Q. Liu, M. Lu, F. Sun, J. Li and Y. Zhao, Oxidation of Benzyl Halides to Aldehydes and Ketones with Potassium Nitrate Catalyzed by Phase-Transfer Catalyst in Aqueous Media, *Synth. Commun.*, **38**, 4188 (2008); https://doi.org/10.1080/00397910802323080
25. G.D. Yadav, P.H. Mehta and B.V. Haldavanekar, Capsule Membrane Phase Transfer Catalysis: Selective Alkaline Hydrolysis and Oxidation of Benzyl Chloride to Benzyl Alcohol and Benzaldehyde, *Stud. Surf. Sci. Catal.*, **78**, 503 (1993); https://doi.org/10.1016/S0167-2991(08)63359-5
26. A.I. Vogel, Text Book of Practical Organic Chemistry, Longman: London (1967).
27. D.D. Perrin, W.L. Armarego and D.R. Perrin, Purification of Organic Compounds, Oxford: Pergamon Press (1966).