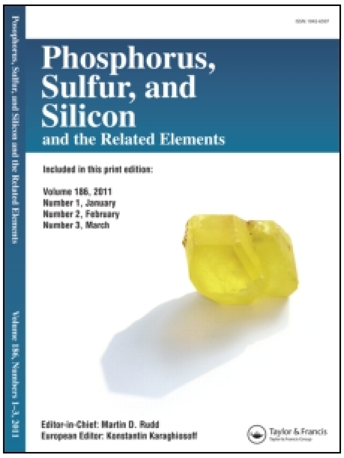

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A New Method for the Oxybromination of Aromatic Compounds with Copper(II)bromide and Potassium Dichromate

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A New Method for the Oxybromination of Aromatic Compounds with Copper(II)bromide and Potassium Dichromate

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A new and mild method for oxybromination of aromatic compounds with $CuBr_2$ and $K_2Cr_2O_7$ in HOAC is reported.

Keywords Aromatic compound; copper(II)bromide; oxybromination; potassium dichromate

INTRODUCTION

The conversion of aromatic compounds to corresponding aromatic halides which are usefull intermediates for preparation of organometallic species is important in organic synthesis and numerous procedures of halogenation such as bromination and chlorination of aromatic compounds in the presence of a catalyst usually ferric bromide or ferric chloride and other lewis acids,[1,2] use of halides of some transition metals,[3–5] chlorination by $Mn(OAC)_3$ and acetylchloride,[6] N-bromosuccinimide and HBF_4,[7] HBr in DMSO[8] and a variety of other bromination methods have been repoted.[9–12] However, many of these suffer from harsh reaction conditions or long reaction times and extraction procedures. Recently the use of oxidants such as oxone[13] and sodium bismutate[14] with metal halides have been used as alternatives for halogenation of aromatic compounds. In this paper we wish to report a simple and convenient procedure for the conversion of aromatic compounds to their corresponding bromides with potassium dichromate as an oxidant and $CuBr_2$ as bromide source.

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TABLE I Oxybromination of Aromatic Compounds with $CuBr_2$ and $K_2Cr_2O_7$ in HOAC

Entry	Substrate	Product	Time (h)	yield[a] (%)
1	Benzene	Bromobenzene	15	65
2	Toluene	p-Bromotoluene	7	87
3	p-Xylene	2-Bromo-1,4-dimethyl benzene	8	70
4	m-Xylene	4-Bromo-1,3-dimethyl benzene	5	65
5	Anisol	p-Bromo anisol	0.5	85
6	Phenol	2,4,6-Tribromo phenol	1	90
7	Acetanilide	p-Bromo acetanilide	0.5	70
8	Aniline	2,4,6-Tribromo aniline	0.5	85
9	Benzaldehyde	—	24	—
10	Benzoic acid	—	24	—
11	Nitrobenzene	—	24	—
12	Cyanobenzene	—	24	—
11	2-Naphthol	1-Bromo-2-naphthol	0.5	80
12	2-Naphthyl amine	1-Bromo-2-naphthyl amine	0.5	85
13	Naphthalene	1-Bromo naphthalene	1.5	88
14	Anthracene	9-Bropmo anthracene	1	90
15	Phenanthrene	9-Bromo phenanthrene	1	92

(a)Yields refer to pure isolated products. Products were characterized by comparison of their physical data, IR and ^{1}HNMR spectra with these of known samples.

RESULTS AND DISCUSSION

When various aromatic substrates were treated with $CuBr_2$ and slight excess of potassium dichromate in acetic acid at ambient temperature, the corresponding aromatic bromides were obtained in good to excellent yields. Work up was conventional and involved dilution of the reaction mixture with dichloromethane, neutralization with sodium bicarbonate solution, and filtration and evaporation of the solvent.The results obtained are summerized in Table I.

The plausible mechanism might be as outlined in Scheme 1.[4]

$$K_2Cr_2O_7 + CuBr \rightarrow Br_2 \xrightarrow{CuBr_2} {}^{+\delta}Br\text{-}Br \ldots Cu^{+}Br_2{}^{-\delta}$$

$$ArH + Br_2 \rightarrow ArBr + HBr$$

$$HBr + CuBr_2 \rightarrow HCuBr_3$$

SCHEME 1

Results in Table I indicate that benzene and its substituted derivatives carring electron-donating groups were converted to the corresponding bromides in moderate to excellent yields (Entries 1–8). Further bromination to di-and tribromo compounds was not obsered except for high reactive aromatic compounds such as phenols and anilines (Entries 6, 8). Substituted derivatives with electron-withdrawing groups either remained intact or gave very poor yields under the same reaction conditions (Entries 11, 12). Bromination of polycyclic aromatic compounds such as naphthalene, anthracene, and phenanthrene were also examined. The reaction of these reactive aromatic moleculs proceeded efficiently and produced bromo compounds in good yields (Entries 13–15). It is noteworthy that the same procedure were carried out with other metal halides such as: $ZnCl_2$, KCl, NaCl, $AlCl_3$, $CaCl_2$, $FeCl_3$ and $MgCl_2$, but only with $CuBr_2$ the reaction afforded high yields.

CONCLUSION

It is evident from the results presented in Table I that our procedure for bromination of aromatic compounds is a mild, convenient, and versatile method and is broadly applicable for the conversion of aromatic compounds into their bromoderivatives.

EXPERIMENTAL

Products were characterized by comparison of their physical data, ^{1}HNMR and IR spectra with those of authentic samples. The purity of products and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica gel polygram SILG/uv 254 plates. All the reagents and solvents used were of AR grade.

GENERAL PROCEDURE

A solution of substrate (5 mmol), copper(II) bromide (5 mmol) and potassium dichromate (5.5 mmol) in glacial acetic acid (5 mmol) in a 100 ml round-bottomed flask equipped with a magnetic stirrer was prepared. The reaction mixture was allowed to stirr at ambient temprature for an approperiate time (Table I). The progress of the rection was monitored by TLC (eluent hexane/ethyl acetate, 10/1). After completion of the reaction, dichloromethane (50 mL) was added to the mixture and the reaction mixture was filtered. The filtrate was washed with water (50 mL × 2) and then with sodium carbonate solution (50 mL × 2). The organic layer after separation was dried over anhydrous sodium sulfate and filtered. The solvent was evaporated. The resulting crude material was purified on a silica gel plate with appropriate solvent. Pure bromo compounds were obtained in 65–95% yields (Table I).

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