



SELECTIVE SYNTHESIS OF BENZOPHENONES BY PHASE TRANSFER CATALYZED MONOCHROMATE OXIDATION OF BENZHYDROLS IN NON-POLAR MEDIA

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ABSTRACT

Selective synthesis of benzophenone and para substituted benzophenones from benzhydrol and corresponding para substituted benzhydrols has been carried out by using acidified monochromate ions as an oxidant in organic medium under phase transfer catalysis. The oxidation reaction was studied at 50°C by magnetic stirring for about two hours in ethyl acetate and toluene as solvents using tetrabutylphosphonium bromide, tetrabutylammonium bromide, tetrabutylammonium hydrogen sulphate, cetyltrimethylammonium bromide and tricaprylmethylammonium chloride as phase transfer catalysts. The reaction is found to be highly selective since no traces of benzoic acids have been detected and the yield of corresponding benzophenones is above 90%. The products obtained on oxidation were precipitated as 2,4-dinitrophenylhydrazone and the recrystallized products were characterized by melting point and by infra-red analysis. From the results obtained, it was found that ethyl acetate is the better solvent and tricaprylmethylammonium chloride is the suitable phase transfer catalyst for this oxidation. The reaction is practically very difficult to proceed in the absence of phase transfer catalyst which proves the significance of phase transfer catalysis technique.

Keywords: Selective oxidation, Benzhydrols, Benzophenones, Monochromate ions, Phase transfer catalysis

1. INTRODUCTION

Oxidation reactions using different oxidizing agents are having great importance in the synthesis of various organic compounds [1-2]. The introduction of phase transfer catalysis (PTC) has brought a revolution in organic synthesis by the anion dissolution in non-polar solvents with their ability to catalyze the reaction. PTC is one of the most efficient methods which can be used to conduct a variety of chemical reactions under mild reaction conditions with notable results. PTC technique is widely used in industry today for attaining the ultimate goals like cost reduction and pollution prevention which are highly significant in the era of green chemistry [3-5]. The commonly used phase transfer catalysts (PT catalysts) are crown ethers and quaternary onium salts in which the latter is more suitable in terms of selectivity, ease of use and low cost [6-8]. Even a little quantity of PT catalyst is enough to transfer the common inorganic oxidants from the aqueous phase to organic phase in the form of ion pairs. The active oxidant in the form of an ion pair in the organic phase reacts with the substrate and forms the product with enhanced rate at optimum conditions. There are reports on oxidation of primary alcohols under PTC using permanganate, chromate,

hypochlorite, hydrogen peroxide etc. as oxidizing agent [9-14]. Hexavalent chromium in various forms are commonly used as mild and selective oxidizing agent in synthetic organic chemistry today under PTC and are mainly used in the oxidation of primary and secondary alcohols to corresponding carbonyl compounds [15-18]. Starks and Liotta had given a detailed explanation on chromate extraction, especially, HCrO_4^- , CrO_4^{2-} , HCr_2O_7^- and $\text{Cr}_2\text{O}_7^{2-}$ into organic solvents using PT catalysts. It was established that under acidic conditions, HCrO_4^- and HCr_2O_7^- were readily phase transferred but the transfer of chromate ions into organic phase will not occur in the absence of acid. According to the present investigation, the dichromate anion, $\text{Cr}_2\text{O}_7^{2-}$ is difficult to be phase transferred into the organic phase and is reported elsewhere [19]. This is due to the difficulty in transferring a bivalent anion. Hence the effective oxidant species which is transferred from aqueous to organic phase is the acidified monochromate ion (HCrO_4^-).

Benzophenone is an important organic compound and is used as a photo initiator in UV-curing applications like inks, imaging and clear coatings in the printing industry. Benzophenone can prevent ultraviolet light from damaging scents and colors in perfumes and soaps and

also added to plastic packaging as a UV blocker to prevent photo-degradation of the packaging polymers or its contents. In biological applications, benzophenones have been extensively used as photophysical probes to identify and map peptide-protein interactions. Benzophenone is commonly produced by the copper catalyzed oxidation of diphenylmethane with air. Laboratory method involves the reaction of benzene with carbon tetrachloride followed by hydrolysis of the resulting diphenyldichloromethane. It can also be prepared by Friedel-Crafts acylation of benzene with benzoyl chloride in the presence of a Lewis acid. All these methods have disadvantages like requirement of high temperature, low yield, formation of by-products etc. The application of PTC method can overcome all the disadvantages faced in conventional methods. The reaction will not occur or be very slow without the use of PT catalysts in both polar and non-polar medium [20-22]. Even though there are reports on such type of oxidation in polar medium, reports using phase transferred monochromate as a selective oxidant in organic solvents is scanty and this prompted us to carry out this work [23-25]. The present paper reports the selective oxidation of benzhydrol and its para substituted derivatives to benzophenone and corresponding para substituted benzophenones by monochromate ions in ethyl acetate and toluene using various PT catalysts such as tetrabutylphosphonium bromide (TBPB), tetrabutyl ammonium bromide (TBAB), tetrabutylammonium hydrogen sulphate (TBAHS), cetyltrimethylammonium bromide (CTMAB) and tricaprilmethylammonium chloride (TCMAC or Aliquat 336) at 50°C.

2. EXPERIMENTAL

2.1. Materials

Analar grade potassium dichromate is used and its solution was prepared in doubly distilled water. Benzhydrol, 4-methoxybenzhydrol, 4-hydroxybenzhydrol, 4-chlorobenzhydrol and 4-bromobenzhydrol (Sisco Research Laboratories Pvt. Ltd., Mumbai) were used as such. The phase transfer catalysts, tetrabutylphosphonium bromide (Merck KGaA, Germany) tetrabutylammonium bromide, Cetyltrimethyl ammonium bromide, tetrabutylammonium hydrogen sulphate and tricaprilmethylammonium chloride (Sisco Research Laboratories Pvt. Ltd., Mumbai) were used as such. The organic solvents toluene and ethyl acetate were purified according to the standard procedure. All the purified solvents were refluxed for 1-2 hours with a

mixture of PT catalyst and potassium dichromate and then distilled [26-27].

2.2. Methods

Selective oxidation of benzhydrols by acidified monochromate ions was carried out in heterogeneous manner. Benzhydrol (0.1 mol) dissolved in 50 mL toluene or ethyl acetate which contains 0.01 mol PT catalyst, was mixed with 50 mL $K_2Cr_2O_7$ (0.5 mol) containing 2 mol dm^{-3} H_2SO_4 . The mixture was stirred vigorously using a magnetic stirrer at 50°C for about two hours. The organic layer was extracted with ether, three times after magnetic stirring. This organic layer was again extracted with 10% sodium bicarbonate and both organic and aqueous layers were separated. A saturated solution of 2,4-dinitrophenylhydrazine in HCl was added to the organic layer and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, recrystallized from ethanol, dried and weighed. The product obtained was analyzed with its melting point and by infra-red spectral technique. The aqueous layer after extraction with sodium bicarbonate was acidified with concentrated HCl. This procedure was repeated with other PT catalysts and using toluene as the solvent. The entire oxidation procedure was also repeated with para substituted benzhydrols.

3. RESULTS AND DISCUSSION

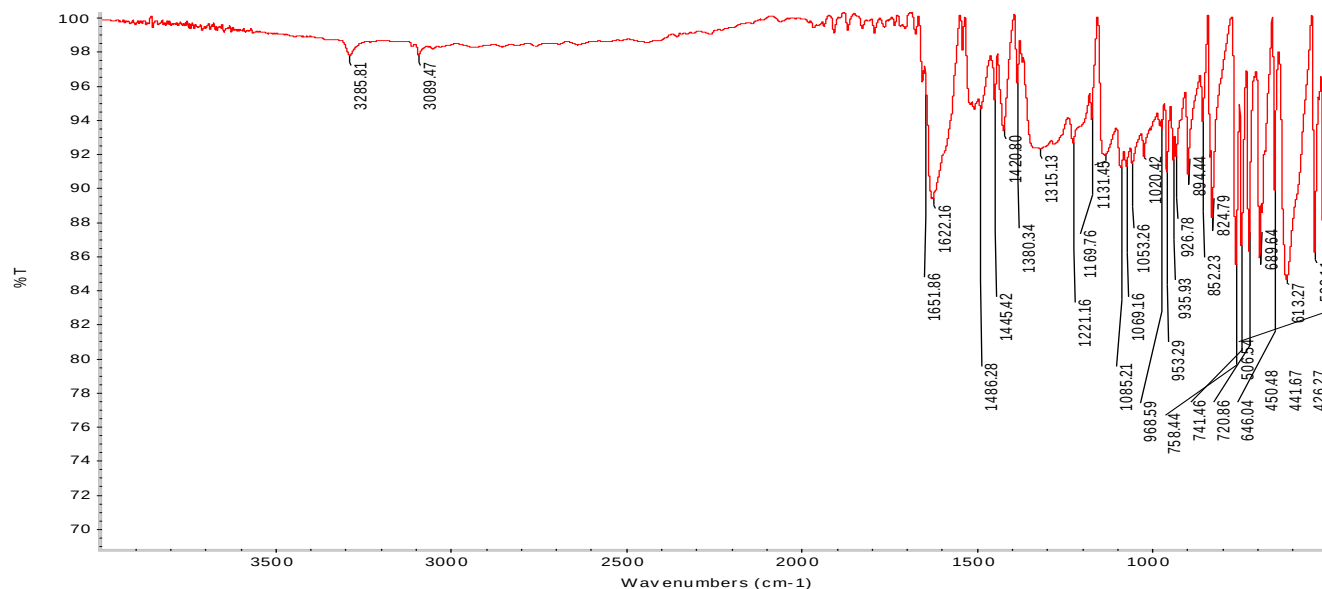
Benzhydrol and para substituted benzhydrols on oxidation with acidified monochromate gave benzophenone and corresponding para substituted benzophenones as the product with high yield (>90%). The recrystallized samples of product obtained were analyzed by its melting point and is given in table 1.

The infra-red absorption spectrum of the product of oxidation of benzhydrol was recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in figure 1.

The infra-red spectrum of the product showed sharp peaks at 1652 cm^{-1} (C=O stretching), 3089 cm^{-1} , (aromatic C-H stretching) and 1651 cm^{-1} (C=C stretching). The existence of all the above peaks established that the product formed may be 2, 4-dinitrophenylhydrazone of benzophenone. Further, the recorded spectrum was compared with that of pure 2,4-dinitrophenylhydrazone of benzophenone available in the literature and found to have excellent similarities.

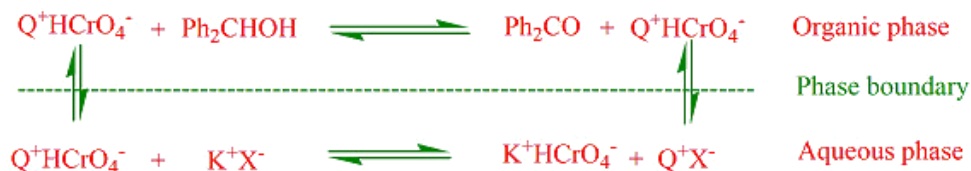
Table 1: Melting points of 2,4-dinitrophenylhydrazone of products (°C) on the oxidation of benzhydrols

Substrate	Melting point of 2,4-dinitrophenylhydrazone of product
Benzhydrol	239 $\pm$ 2
4-chlorobenzhydrol	183 $\pm$ 2
4-bromobenzhydrol	232 $\pm$ 2
4-methoxybenzhydrol	182 $\pm$ 2
4-hydroxybenzhydrol	240 $\pm$ 2

**Fig. 1: Infra-red spectrum of product on oxidation of benzhydrol**

The product obtained on the monochromate oxidation of benzhydrol and its para substituted derivatives under PTC in organic solvents were identified as benzophenone and corresponding para substituted benzophenones with very high yield. This method is significant in terms of selectivity since no traces of acid or other products were formed during the reaction at any stage. The reaction proceeded smoothly in both the solvents namely ethyl acetate and toluene. But the yields of benzophenones were found to be more in ethyl acetate than that in toluene. This may be due to the higher polarity of ethyl

acetate than toluene. Polarity of the solvents helps in increasing the solubility and partitioning of quaternary salts. Various PT catalysts were used in the reaction and all of them function well in the oxidation. There is a slight difference in the yield and ease of reaction with respect to PT catalyst and is in the order TCMAC > TBPB > TBAB > TBAHS > CTMAB. This is attributed to the changes in combination of alkyl groups or may be to the difference in the activity of anions for phase transfer reaction. The reaction path for the monochromate oxidation of benzhydrols under PTC is given scheme 1.

**Scheme 1: Phase transfer catalytic cycle for the oxidation of benzhydrols**

4. CONCLUSIONS

In summary, a simple, efficient and a selective green method for the conversion of benzhydrols to benzophenones under phase transfer catalysis in organic solvents was reported. Acidified monochromate ions were found to be very effective and selective oxidant in the oxidation of benzhydrols under PTC with very high yield. Greener solvents were used for this conversion and there was no formation of by-products during the entire reaction process. So, this method under PTC can be adapted to other reaction systems and also under solvent free conditions.

5. REFERENCES

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