

zirconium in the heteropolyacid was established to be 12:1:1 by the isomolar series method proposed by Babko³.

Interference studies: The interfering effect of one milligram amount of several cations and anions in the determination of zirconium are shown in table 1. A deviation of more than ± 0.02 from the absorbance of the solution without any interfering ion was taken as a sign of interference.

TABLE 1

Interference studies (Zirconium 2 ppm).

Ions	Remarks
1. Ca, Mg, Cu(II), Co(II), Ni, Zn, Hg(II), Cd, Al, Be, Mn(II) NO ₃ ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , SO ₄ ²⁻ , ClO ₄ ⁻ , acetate	No interference upto 1 mg level
2. Pb, Sr, Ba	Interfered by precipitation
3. Fe(III), Ce(IV), Ti(IV), Th, W(VI); V(V), Hf, U(VI), PO ₄ ³⁻ , SiO ₃ ²⁻	Interfered by increasing the
4. Sn(II), F ⁻ , citrate, tartrate, oxalate, EDTA	Interfered by decreasing the absorbance

The interference due to Ba, Pb and Sr was no longer noticed when the absorbance measurements were made after removing the precipitate by centrifugation. The interference of tin(II) was overcome by boiling with bromine water prior to the addition of ammonium molybdate and arsenate. Addition of 2 ml of 1% solution of beryllium sulphate prior to the addition of ammonium molybdate overcame the interference of fluoride. The interference due to phosphate, silicate and tungstate was removed by extraction of their heteropolymolybdates in 1:1 mixture of isobutylmethyl ketone and *n*-butanol at pH 1.0 in the absence of sodium arsenate. After extraction, colour was developed by reacting with sodium arsenate after adding a further quantity of 5 ml of ammonium molybdate and following the usual procedure. The interference due to titanium and uranium were overcome by coprecipitating zirconium with iron(III) hydroxide in the presence of one gram of ammonium chloride and 2 ml of 6% hydrogen peroxide at pH 4.0. The precipitate was repeatedly washed with dilute ammonium carbonate solution and then dissolved in 1:1 hydrochloric acid. After the removal of iron(III) by extraction with ether the aqueous layer was evaporated to dryness dissolved in 20 ml water and the estimation was carried out as described already.

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CERIUM (IV) INDUCED ONE POT SYNTHESIS OF 2,4-DIHYDROXY-3-NITRO ACETOPHENONE—A MODEL FOR BIOMIMETIC AROMATIC HYDROXYLATIONS

H. MOHINDRA CHAWLA AND RAM S. MITTAL
Department of Chemistry, Indian Institute of Technology, New Delhi 110 015, India.

HYDROXYLATION of aromatic hydrocarbons is one of the most important reactions in biomimetic organic chemistry. Various attempts have been made to introduce a hydroxyl group into aromatic hydrocarbons by means of enzymes and using hydrophobic and hydrophilic catechols in the presence of ferric ions and hydrogen peroxide¹. Such models achieved little practical success but nonetheless are important in establishing some of the enzymatic processes in the living cell². Recently Barton and coworkers during their investigation on tetracycline synthesis, have hinted upon the plausible similarity between cerium dioxide (CeO₂) and hydrogen peroxide system to that involving singlet molecular oxygen³ and since we were engaged in studies involving singlet molecular oxygen as a model for dioxygenases to mimic natural processes in polyphenols^{4,5}, we were interested in studying the efficacy of cerium compounds in biomimetic hydroxylations and developing simpler methods for obtaining difficultly accessible poly hydroxy benzenes.

One of the conventional ways of introducing hydroxyl group in benzene ring is *via* nitration, reduction and diazotisation. This process, though very much feasible has limitations because of the facile oxidation of phenols when treated with the nitrating agent instead of getting nitrated. Thus it seems imperative to develop methods for achieving chemoselective processes to get mononitrophenols which then can be converted to polyhydroxy benzenes by conventional methods. In our preliminary experiments, we have achieved a convenient synthesis of 2-nitro-1,3,4-trihydroxy benzene in good yields which can then be converted to 1,2,3,4-tetrahydroxy benzene. To get 2-

nitro-1,3,4-trihydroxy benzene pyrocatechol cannot be used for nitration because of its facile oxidation. Resorcinol too was a poor choice for nitration experiment because in resorcinol, it is the β -position that is more reactive towards substitutions rather than the γ -position. Good yields of γ -substituted resorcinol derivatives are difficult to realise. Resacetophenone also leads to electrophilic substitutions in position 5 by most of the conventional reagents. In our experiments towards biomimetic hydroxylations, we have achieved the synthesis of 2,4-dihydroxy-3-nitro-acetophenone in good yield by the reaction of cerium (IV) ammonium nitrate, a well documented reagent for oxidations^{6,7} and oxidative acetoxylation^{8,9}. 2,4-dihydroxy-3-nitroacetophenone can then be conveniently oxidised by Baeyer Villiger reactions to yield 2-nitro-1,3,4-trihydroxy benzene, a model for tetrahydroxy benzenes.

This communication is the first one pot facile synthesis of 2,4-dihydroxy-3-nitroacetophenone in good yields. Further work on the mechanism and applications of the reagent for oxidation in hydrophobic and hydrophilic phases is in progress.

Resacetophenone (2 g) in acetic acid (5 ml) was added to a solution of cerium (IV) ammonium nitrate in acetic acid (5 g, 30 ml) and the reaction mixture heated in water bath (50–60°, 5 min). The progress of the reaction was followed by TLC; on its completion (20 min) the reaction mixture was poured on to crushed ice (50 g) and extracted with benzene, the organic layer on concentration left a solid which was column chromatographed (silica-gel) using petroleum ether and benzene for elution. A shining yellow compound A was obtained from the petroleum ether-benzene (95:5) eluate which melted at 90–91° C, gave positive Lassaigne's test for nitrogen and positive ferric reaction for phenols. It showed strong absorptions at 3200 cm^{-1} (-OH group) and 1520, 1320 cm^{-1} (nitro group) in its IR spectrum and a two proton singlet at δ 12.4 attributable to two phenolic protons; a two proton multiplet at δ 8.0 assignable to aromatic protons and a singlet at δ 2.6 integrating for 3 protons (COCH_3) in its PMR spectrum. The identity of compound A was established as 2,4-dihydroxy-3-nitro-acetophenone by comparison with its literature data (lit m.p. 93° C). Compound A on treatment with $\text{H}_2\text{O}_2/\text{OH}^-$ gave 2-nitro-1,3,4-trihydroxy benzene (m.p., m.m.p., Co-IR and Co-TLC) with authentic sample in 20% yield.

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KINETICS OF AQUATION OF BROMOPENTA-AMMINECOBALT (III) PERCHLORATE IN DICARBOXYLATE SOLUTIONS CONTAINING 10% ETHANOL AT 40° C.

M. F. AMIRA*, F. M. ABDEL-HALIM,
N. H. ISMAIL AND M. M. ELSEMONGY†
Chemistry Department, Faculty of Science,
Alexandria University, Egypt.

*Present address: Chemistry Department, Faculty of Science, Sana'a University, Yemen Arab Republic.

† Chemistry Department, Faculty of Science, Mansoura University, Egypt.

RECENTLY Amira, *et al*¹ surveyed studies on the rate of aquations of chloro-and bromo-penta-amminecobalt (III) and of penta-amminechromium (III) in aqueous and also in the presence of 10% ethanolic solutions of sulphate and dicarboxylates. They found an exception in the empirical correlation between $k(\text{ion-pair})/k(\text{ion})$ (k_{ip}/k_i) ratio and the dissociation constants (K) for the dicarboxylate series in the case of aquation of bromopenta-amminecobalt (III) ion in 10% ethanolic dicarboxylate solutions. This was attributed to the consequence of using a mixed solvent.

In our present investigation, a comprehensive study was undertaken on the kinetics of aquation of bromopenta-amminecobalt (III) perchlorate in 10% ethanolic dicarboxylate solutions to solve the above exception.

Bromopenta-amminecobalt (III) bromide was prepared² and converted to perchlorate from warm acidi-