

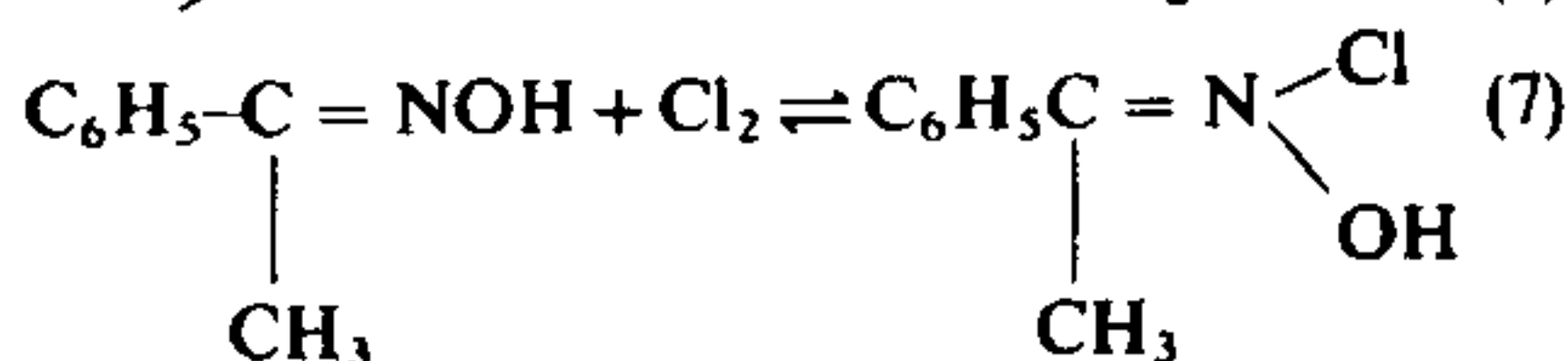
**Table 3** Effect of substituents in the oxidation of APO by CBT

	$k_t \times 10^4$ 303 K	$\text{sec}^{-1}$ 308 K
Acetophenone oxime	2.85	5.02
<i>p</i> -Chloroacetophenone oxime	2.07	2.17
<i>p</i> -Bromoacetophenone oxime	2.24	2.72
<i>p</i> -Methylacetophenone oxime	4.01	6.84
<i>p</i> -Methoxyacetophenone oxime	5.79	7.76

[CBT] =  $1.0 \times 10^{-3}$  M [oxime] =  $1.0 \times 10^{-2}$  M  
Solvent = 50% HOAc - 50% H<sub>2</sub>O.

stituents increase the reaction rate and the electron-withdrawing substituents decrease it.

In the presence of chloride ion the following mechanism is proposed in addition to scheme 1.



The protonated CBT reacts with Cl<sup>-</sup> to form free chlorine which reacts with acetophenone oxime at a faster rate and follows the steps 3, 4 and 5 as in scheme 1.

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### A NOVEL OBSERVATION ON THE REACTION OF 1,4-DIACETOXYBENZENE(III) WITH CERIUM(IV) AMMONIUM NITRATE

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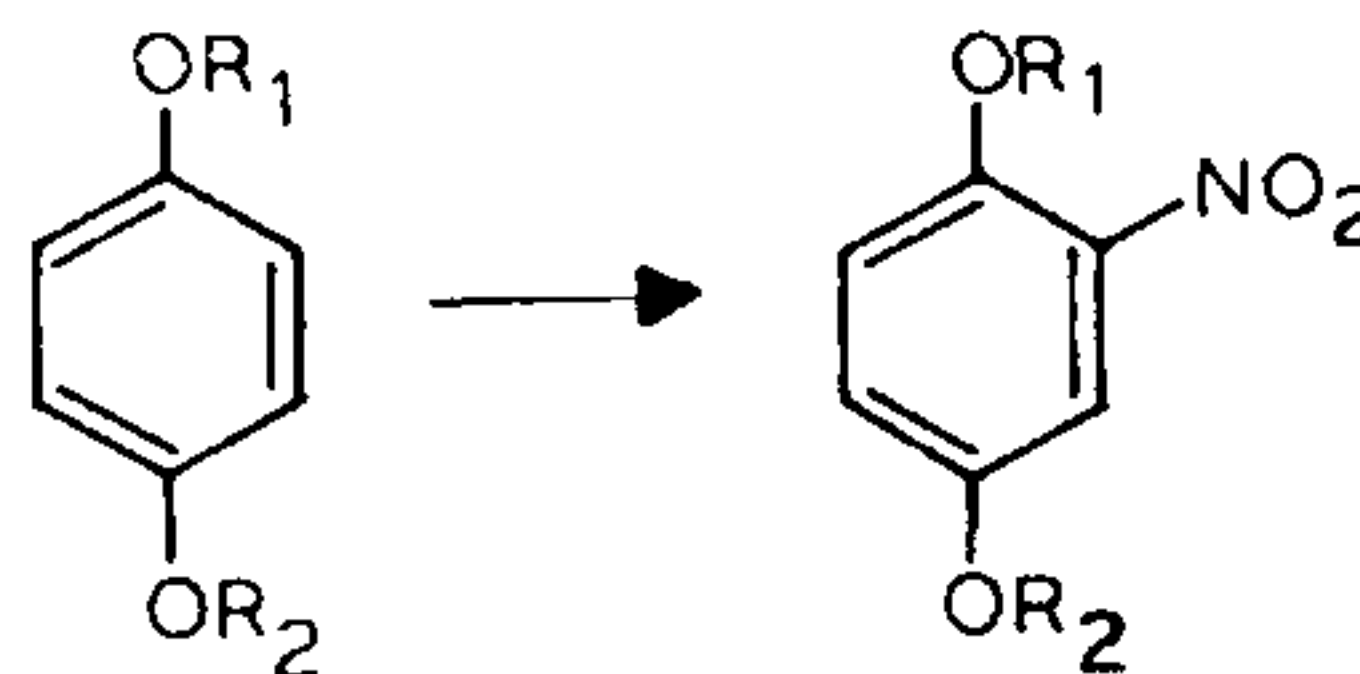
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IN continuation of our study on the reaction of phenolics induced by ceric ammonium nitrate (CAN)<sup>1,2</sup>, we have now studied the reactions of 1,4-dihydroxy; 1,4-dimethoxy; and 1,4-diacetoxybenzene with CAN. It is interesting to note that contrary to 1,4-dihydroxy and 1,4-dimethoxybenzenes where oxidation product is only quinone, no such oxidation product was obtained in 1,4-diacetoxybenzene, instead, nitro and deacetylated nitro products (IV and V) were obtained. This is the first report of nitration and deacetylation of diacetylbenzene using CAN as a reagent.

#### Experimental procedure

The phenol (1 g) was treated with CAN (2.2 g; 4 m mol) under conditions given in table 1. After the



- |     |                          |    |                                    |
|-----|--------------------------|----|------------------------------------|
| I   | $R_1 = R_2 = \text{H}$   | IV | $R_1 = \text{H}, R_2 = \text{OAc}$ |
| II  | $R_1 = R_2 = \text{OMe}$ | V  | $R_1 = R_2 = \text{H}$             |
| III | $R_1 = R_2 = \text{OAc}$ |    |                                    |

**Table 1** Reactions of phenolic substrates with CAN and their products

Substrate	Solvent	Reaction conditions	Product	Yield %
I	Acetonitrile	20°, 0.5 hr	Benzoquinone	60
II	Acetonitrile:	20°, 1.5 hr	Benzoquinone	70
	water (2:1)			
III	Methanol:	60°, 4 hr	IV	40
	acetic acid			
	(1:1)		V	50

reaction is completed the mixture was diluted with ice cold water and exhaustively extracted with ethyl acetate. The organic extract was then concentrated and subjected to column chromatography over silica gel using petroleum ether, benzene and ethyl acetate either alone or in binary mixtures and the products obtained in pure state were identified by comparison with authentic samples.

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## POLYMER SUPPORTED REAGENTS: A SIMPLE AND EFFICIENT METHOD FOR BENZOYLATION OF PHENOLS

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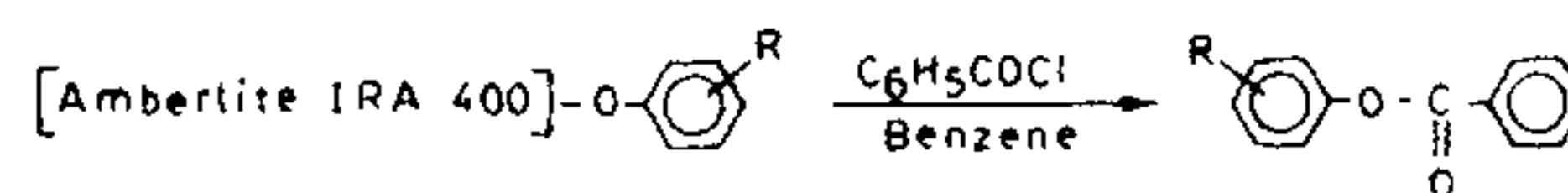
THE synthesis of benzoyl ester has many uses in organic chemistry. A majority of benzoyl esters are solids and as such, they provide a useful means of characterizing phenols.

Benzoyl ester may be prepared according to the traditional method by treatment of phenol with benzoyl chloride in presence of alkali; however if benzoyl ester is soluble in alkali, it requires tedious reaction work-up resulting in low yields<sup>1</sup>.

The reagents supported on insoluble polymers have found wide application during the last decade in various fields, particularly, in organic synthesis<sup>2</sup>. In continuation of our work on polymer supported reagents<sup>3-5</sup> and in view of the importance of benzoyl esters as a protecting group<sup>6-8</sup>, a simple and efficient method is now reported for the synthesis of the same in quantitative yield and purity under mild reaction conditions in nonaqueous medium.

This method has the advantage of higher yields and simplicity of performance. This method is inexpensive as the resin could be used repeatedly and it can be regenerated to its initial activity by treatment with hydrochloric acid. Reaction with catalytic amount of the resin does not give satisfactory results. Thus, the nucleophilicity of the polymer-bound phenoxide ion is increased sufficiently to allow the reaction with benzoyl chloride in a manner which is related to the principles of phase transfer technique with low molecular catalysts. Representative substituted phenoxides are summarized in table 1.

Typical procedure for the preparation of polymer supported phenoxide:- Commercial, strongly basic anion exchange resin in chloride form [Amberlite IRA-400 (Cl<sup>-</sup>)] packed in a column is washed with 0.25 N aqueous sodium salt of phenol until complete removal of chloride ion. The resin is then successively washed with water and ethanol and is finally dried in vacuum at 50°C over P<sub>2</sub>O<sub>5</sub> for 10 hr. The exchange capacity is determined by passing aqueous 1 M sodium chloride solution (100 ml) through the resin (0.3 g) in a column. The amount of phenoxide in the eluent is titrated with

**Table 1** Benzoyl ester

Phenol	Yield (%)
Phenol	95
<i>o</i> -Cresol	92
<i>p</i> -Cresol	92
<i>o</i> -Nitrophenol	91
<i>p</i> -Nitrophenol	95
<i>o</i> -Chlorophenol	95
<i>p</i> -Chlorophenol	95
$\beta$ -Naphthol	90
4-Methyl-7-Hydroxycoumarine	90
Methyl salicylate	90
Ethyl salicylate	90
Methyl <i>p</i> -hydroxybenzoate	90