

# Design and Applications of a Solid-Phase Oxidizing Reagent Consisting of a Crosslinked Polystyrene Matrix and a *t*-Butyl Hypochlorite Function Separated by a Trimethylene Spacer

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## Synopsis

A crosslinked polystyrene-supported solid-phase analogue of *t*-butyl hypochlorite containing a trimethylene spacer group between the polymer matrix and the *t*-butyl hypochlorite function was prepared and used as a recyclable oxidizing reagent for alcohols. The synthetic route to this new polymeric reagent involved a seven-step polymer-analogous reaction starting from styrene-divinyl benzene 2%-crosslinked polymer. A  $\beta$ -ketopropionic acid function was introduced into the polystyrene matrix by Friedel-Crafts reaction with succinic anhydride. The keto function in the resulting polymer (2) (capacity, 3.57 meq of  $\text{COCH}_2\text{CH}_2\text{COOH/g}$ ) was converted to the methylene group by Clemmensen reduction using zinc amalgam and HCl. The carboxyl function in the product polymer (3) was converted to the acylmalonic ester function by malonic ester synthesis through the reaction of the polymeric acid chloride (4) with ethoxymagnesium diethylmalonate. The polymeric acyl malonic ester (5) was decarboxylated to yield the 2-oxopentyl polystyrene resin (6). This on Grignard reaction with methyl magnesium iodide followed by hydrolysis afforded the polystyrene derivative with the *t*-butyl alcohol function separated by three methylene groups (7). The *t*-butyl alcohol resin (7) was converted to the corresponding hypochlorite resin (8) by reaction with sodium hypochlorite. The resin was found to have a capacity of 2.84 mmol Cl/g by iodometric analysis. The capacities of the resins 2–8 were determined from the weight changes in the corresponding conversions and verified by quantitative determination of the functional groups. This new hypochlorite was found to oxidize alcohols to carbonyl compounds in 85–98% yield. The oxidizing efficiency of this new reagent was found to be significantly greater than those of the reagents containing only one spacer and no spacer between the reagent function and the polymer support. The presence of a 3-methylene spacer also facilitated the hypochlorite formation step significantly.

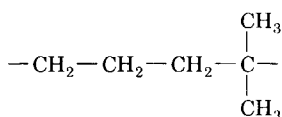
## INTRODUCTION

The use of crosslinked polymeric supports in the design of solid-phase organic reagents<sup>1,2</sup> continues to be an active field of investigation ever since the introduction of the polymer-supported solid-phase method by Merrifield.<sup>3,4</sup> A polymeric organic reagent can provide an effective alternative to its low-molecular weight counterpart if its design is such that it allows for an easier isolation of the desired product after the reaction and if the polymeric by-product can be regenerated and recycled for further use without loss of

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reactivity.<sup>5,6</sup> These immobilized reagents are similar in behavior to their low-molecular weight analogues, but have the inherent advantage of insolubility. In solvent-swollen reactive polymers, the microenvironment of the reactive site would appear to be the same as that of the reactants in solution; however, the bulkiness of the insoluble phase imposes steric constraints on the transition state which may lead to regio- and/or stereospecific reactions. The high local concentration of reagents in the polymer matrix influence the kinetics. The advantages of homogeneous and heterogeneous reactions are thus combined.

As part of a program to investigate the feasibility of attaching the *t*-butyl hypochlorite function onto the insoluble polystyrene backbone and the use of this as an oxidizing and halogenating reagent, eliminating the toxic and hazardous nature of these otherwise versatile reagents, we have recently reported a polystyrene-supported analogue of the *t*-butyl hypochlorite and hypobromite.<sup>7</sup> The synthetic utility of these solid-phase reagents was demonstrated by their application as recyclable oxidizing and halogenating agents for organic substrates. However, the reactivity of the system was found to be much less compared to that in the reaction with the low-molecular weight substrate. Preliminary investigations indicated that this drastic reduction in reactivity is an effect of the immediate neighborhood of the crosslinked polystyrene matrix to the hypochlorite function. Therefore, we thought of modifying the structural environment of the hypochlorite reaction site so that it protrudes away from the polymer backbone. Thus, the present paper describes the synthesis of a crosslinked polystyrene with the hypochlorite function separated by the group

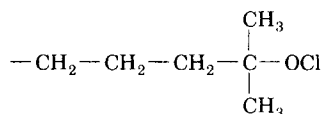


and its efficiency as oxidizing reagent.

## RESULTS AND DISCUSSIONS

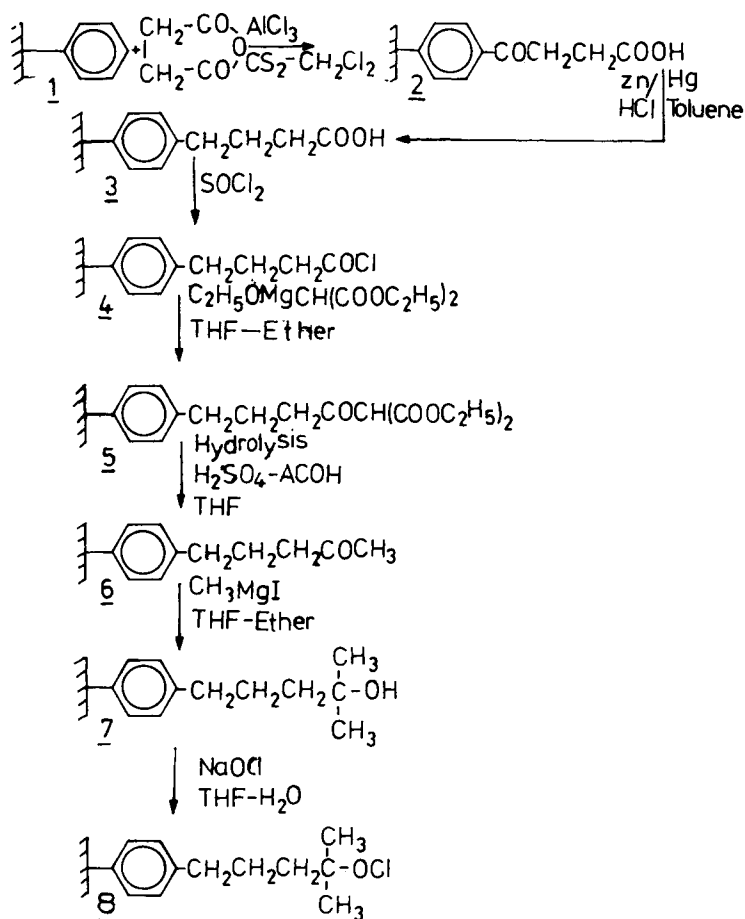
### Preparation and Characterization of the Reagent

The preparation of polymeric reagent containing a



function was accomplished by a seven-step polymer analogous reaction starting from 2%-crosslinked styrene-DVB copolymer (Scheme I). A ketonic acid function,  $\beta$ -ketopropionic acid, was introduced into the crosslinked polystyrene beads (1) by Friedel-Crafts reaction with succinic anhydride. The reaction was followed by the appearance of intense carbonyl and carboxyl absorptions

at  $1690\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching) and  $1450\text{ cm}^{-1}$  ( $\text{C}-\text{O}$  str.) in the IR spectrum. This keto acid resin (**2**) was reduced with  $\text{Zn}/\text{Hg}$  and  $\text{HCl}$  to afford the resin (**3**) with the butanoic acid function. The band at  $1690\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  str.) became weak and that at  $1450\text{ cm}^{-1}$  persisted still. The polymer (**3**) was converted to the acid chloride resin (**4**) by treatment with thionyl chloride. This polymer was characterized by a strong absorption band at  $1810\text{ cm}^{-1}$ . The acid chloride resin was subjected to malonic ester-type synthesis using ethoxy magnesium diethyl malonate followed by hydrolysis with sulfuric acid/acetic acid mixture to afford the resin (**5**) with IR absorption bands at  $1450\text{ cm}^{-1}$  ( $\text{C}-\text{O}$  str.),  $1650\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ , ester) and  $3300\text{ cm}^{-1}$  ( $\text{CH}$  str.). On hydrolysis, (**5**) afforded the resin (**6**) with the ketone function  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{COCH}_3$ , characterized by an intense absorption band at  $1740\text{ cm}^{-1}$ . Grignard reaction of (**6**) with methyl magnesium iodide followed by hydrolysis resulted in the formation of the tertiary alcohol resin (**7**). The absorption band at  $1740\text{ cm}^{-1}$  disappeared completely in this case. The tertiary alcohol resin on reaction with sodium hypochlorite yielded the hypochlorite resin (**8**).



Scheme I.

In all the above steps of the reaction, a considerable dependence of the extent of conversion on the nature of the solvent was observed. This effect was highly prominent in the Friedel–Crafts reaction step with the succinic anhydride. The reaction was conducted in nitrobenzene, a mixture of nitrobenzene and carbon tetrachloride, carbon tetrachloride, carbon disulfide, and a mixture of carbon disulfide and methylene chloride as solvents. A fourfold increase in capacity with respect to the  $-\text{COCH}_2\text{CH}_2\text{COOH}$  was observed on changing the solvent from nitrobenzene to a mixture of carbon disulfide and methylene chloride. The polystyrene resin was found to swell maximum in carbon disulfide. But the solubility of succinic anhydride–Lewis acid complex was found to be less in carbon disulfide and methylene chloride. Thus this mixture of solvents was found to be most suitable for carrying out the Friedel–Crafts reaction. The Clemmensen reduction step was most effective in toluene. The resin undergoes effective swelling in this solvent. The reduction reaction using Zn–Hg/HCl being a heterogeneous one, it is not fully clear how this heterogeneous reagent penetrates so effectively into the solvent-swollen resin. It is likely that the reaction in the gel-phase provides maximum penetration to the heterogeneous reagent. The low-molecular weight Clemmensen reduction is carried out in a three-phase system in which most of the substrate remains in a hydrocarbon layer, and the protonated carbonyl compound in the aqueous layer is reduced on the metal surface. The most suitable solvent for the malonic ester-type synthesis step was THF. The hydrolysis of resin (5) to give resin (6), Grignard reaction on resin (6) and the hypochlorite conversion step occurred most efficiently in terms of yield and reaction periods when the reactions were carried but in the presence of THF. These observations point to the role of “good solvents” in swelling the hydrophobic polystyrene matrix.

The resins with the different functional groups retained their bead form characteristic of styrene–divinyl benzene copolymers prepared by suspension polymerization.<sup>8</sup> Depending upon the duration of mechanical stirring, attrition of the resins was observed in some cases. In certain stages some mechanical loss was also observed due to powdering. This resulted in slow filtration during the washing and work-up processes. The chlorine content of the hypochlorite resin was determined by iodometric titration and verified by the modified Volhard’s method and total halogen elemental analysis. The chlorine content of the hypochlorite resin was found to be 2.84 mmol Cl/g. The capacities of the resins 2–8 were determined from the weight changes in the corresponding functional group conversions and verified by quantitative determination of the functional groups. The carboxylic group in resin 2 and 3 were estimated by alkalimetric titrations. The reduction of resin 2 to form the resin 3 was gravimetrically followed based on the 2,4-dinitrophenyl hydrazone formation of the ketonic resin 2. The acid chloride resin 4 was estimated by Volhard’s method. From the weight increase the capacity of the resin should be 4.25 meq/g which was found to be greater than 3.05 meq/g, the value obtained from the Volhard method. The reasons for this discrepancy are the extreme difficulty in completely removing the solvents in the drying process in the case of the highly swellable resins and the unavoidable errors in the weighing process. Even after many hours (3–4 h) of vacuum drying, some of the resins contain 5–10% of the solvent. The capacities of the resins 5, 6, and 7, were determined by following the weight differences.

## Oxidation of Alcohols Using the Hypochlorite Resin (8)

The hypochlorite resin (8) was found to oxidize alcohols to corresponding carbonyl compounds in near quantitative yields. Primary alcohols were oxidized to aldehydes and secondary alcohols to ketones in isolated yields ranging from 85 to 98%. The oxidation conditions involve stirring of the alcohols with a two-fold molar excess of the hypochlorite resin in chloroform at room temperature. The resin was removed from the reaction mixture by filtration after reaction and washed with chloroform. Removal of the solvent from the combined filtrate and washings afforded the product. The reaction was followed by thin layer chromatography. The details of the oxidation reactions carried out by the hypochlorite resin are given in Table I.

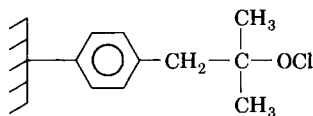
Striking differences were observed in the oxidation reactions with this new polymeric reagent from the reactions with the hypochlorite resins we reported earlier.<sup>7</sup> For the hypochlorite resin (9) with one methylene group between the hypochlorite function and the polymer backbone, the minimum time required for completion of the reaction was 43 h, on an average. With this resin after 24 h, conversion to carbonyl compounds was found to be less than 50%. But with the resin (8) the duration of the reaction was reduced to 30 h for complete conversion. After 24 h, almost full conversion occurred. With the resin (10), in which the hypochlorite function is nearest to the polymer

TABLE I  
Oxidation of Alcohols Using *t*-Butyl Hypochlorite Resins

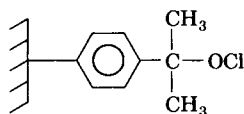
Alcohols	Resin 9 <sup>a</sup>		Resin 10 <sup>a</sup>		Resin 8 <sup>a</sup>	
	Reaction period <sup>b</sup> (h)	Isolated yield (%)	Reaction period <sup>b</sup> (h)	Isolated yield (%)	Reaction period <sup>b</sup> (h)	Isolated yield (%)
Benzyl alcohol	43	98	72	86	30	98
<i>n</i> -Butyl alcohol	40	90	72	90	30	96
Cyclohexanol	42	89	72	79	30	92
Cholesterol	40	98	96	81	30	96
Menthol	43	83	72	78	30	87
Benzoin	40	77	72	76	30	82

<sup>a</sup> Twofold molar excess.

<sup>b</sup> Includes preswelling also:



9



10

backbone, an average period of 96 h was required for 80% conversion. These comparisons are made for the case of the cholesterol-to-cholestenone oxidation reaction.

When the comparison of the reactivity of the hypochlorite function in the three resins was made as a function of the ratio of the amounts of the resin and the alcohol for the completion of the reaction, similar results were obtained. When the resin-to-alcohol ratio was 2.8:1 in the case of the new resin, the reaction was complete within 30 h. The resin after the oxidation reaction contained 1.02 mmol residual chlorine/g resin. Thus in this case, only 1.78 mmol of chlorine was consumed for 1 mmol of alcohol. With the hypochlorite resin (**9**) containing one spacer methylene group, the same resin-to-alcohol ratio gave complete conversion only after 43 h. The residual chlorine content of the resin was only 0.78 mmol chlorine/g resin. Here apparently 2.02 mmol of chlorine was consumed for 1 mmol of alcohol. Under identical conditions, the resin (**10**), with no spacer in between the hypochlorite function and the polymer backbone, yielded only 0.28 mmol residual chlorine/g after 72 h of reaction, corresponding to a consumption of 2.52 mmol Cl/mmol alcohol. In all these cases, the reaction was carried to completion to facilitate the work-up procedure.

The product isolation and purification steps were made easy by the fact that no products of overoxidation (acids in the case of primary alcohols) or chlorinated products (arising from the possibility of chlorination under some conditions<sup>7</sup>) were found in the reaction mixture once the oxidation was complete. Thus the carbonyl compounds were obtained by a simple filtration followed by washing of the resin to extract all the product and evaporation of the solvent.

The effect of the spacer methylene groups was also observable in the extent of the polymer-analogous conversions and on the capacity of the hypochlorite resin. Thus the reaction of sodium hypochlorite with the tertiary alcohol resin (**7**), where the hydroxyl group was separated from the polystyrene matrix by three methylene groups, yielded a hypochlorite resin (**8**) having a capacity of 2.84 mmol Cl/g resin. This required a reaction time of 24 h. When the hydroxyl was separated by one methylene group, the capacity of the hypochlorite resin was 2.33 mmol Cl/g after a reaction period of 24 h. But when the hydroxyl group was attached to the carbon nearest to the polymer matrix, for a maximum capacity of 1.23 mmol Cl/g the reaction period was 120 h. These observations point to the fact that the spacer arm projects the active functions into the solution phase where it could effectively react with the low-molecular-weight substrate, thereby increasing the reaction efficiency. This observation is consistent with the earlier observations with regard to phase-transfer catalysts.<sup>9-11</sup>

### Recyclability of the Spent Resin

The resins recovered after the oxidation reactions were collected and washed thoroughly with different solvents. Treatment of the recovered resin suspended in tetrahydrofuran with freshly prepared sodium hypochlorite regenerated the hypochlorite resin. The regenerated resin retained the same functional group capacity and physical features as the original resin. The

TABLE II  
Oxidation of Benzoin Using Regenerated and Recycled Hypochlorite Resins

No. of cycles	Capacity (meq/g)	Time of reaction <sup>a</sup>	Yield
1	2.84	30	82
2	2.79	30	82
3	2.74	30	82
4	2.71	30	82
5	2.67	30	80

<sup>a</sup>Twofold molar excess of the resin used.

recycled resin was found to be equally efficient in carrying out oxidation reactions. In the present study the resin was recycled four times without appreciable loss of capacity or activity. The oxidation of benzoin to benzil was employed in the recycling experiments. The details of the oxidation reaction using the resins which are recycled up to four times are given in Table II.

Thus the new hypochlorite oxidizing agent consisting of a crosslinked polystyrene matrix and a *t*-butyl hypochlorite function separated by a trimethylene spacer was found to possess the desired characteristics of polymeric reagents including operational simplicity, filterability, and recyclability. The reaction efficiency was found to be retained for many cycles of operation without any chemical degradation of the polymer. The only loss observed during all these processes was mechanical due to powdering, which was unavoidable in the magnetic stirring process and due to repeated transfers of the polymer. Studies are in progress to establish the utility of these new reagents for halogenation of ketones and amides and to elucidate the effect of crosslinking, temperature, etc. on the nature of the reactions.

## EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer spectrometer using KBr pellets. Solvents were purified by standard procedures. The resin support used was 2%-crosslinked styrene-divinyl benzene macroporous beads prepared by suspension copolymerization or purchased from Aldrich Chemical Co., West Germany. All the low-molecular weight substrates used were commercially available samples purified by distillation or crystallization. Succinic anhydride<sup>12</sup> and ethoxymagnesium diethyl malonate<sup>13</sup> were prepared following literature procedures.

### Friedel-Crafts Reaction of Polystyrene (1) with Succinic Anhydride: Preparation of the Ketonic Acid Resin (2)

Two-percent-crosslinked styrene-divinyl benzene copolymer beads were thoroughly washed with chloroform and methylene chloride and dried in vacuum. To a suspension of the resin (10 g), preswollen (10 h) in nitrobenzene,

a previously prepared solution of succinic anhydride (14 g) and anhydrous aluminium chloride (20 g) was added with good stirring for a period of 10 min.\* The reaction mixture was heated under reflux for 6 h at 80°C. After cooling, water (100 mL) was added, and the resin particles were filtered at the pump, washed successively with water, methanol, chloroform, and acetone, drained and dried. Yield, 11.02 g; capacity with respect to the  $-\text{COCH}_2\text{CH}_2\text{COOH}$  function, 2.75 meq/g. The reaction was repeated using different solvents. The yield and capacity of the product resin in these solvent systems are: nitrobenzene-carbon tetrachloride (1 : 1 v/v), yield 12.5 g, capacity, 3.125 meq/g; carbon disulfide-methylene-chloride (4 : 1 v/v), yield, 14.25 g, capacity, 3.57 meq/g. The product showed intense absorption bands at  $1690\text{ cm}^{-1}$  (C=O str.) and  $1450\text{ cm}^{-1}$  (C—O str.). The presence of the ketonic acid function was detected by the reaction with sodium bicarbonate in aqueous THF and by the formation of the 2,4-dinitrophenyl hydrazone derivative.

### **Clemmensen Reduction of Poly(styryl B-Keto Propionic Acid) (2)**

#### **(Capacity: 3.57 meq / g); Formation of Poly(styryl Butyric Acid) (3)**

Amalgamated zinc was prepared by shaking a mixture of 120 g of mossy zinc, 12 g of mercuric chloride, 200 mL of water and 5–6 mL of concd HCl for 5 min. The supernatant solution was decanted and washed, and the zinc amalgam used immediately.

Seventy-five milliliters of water, 175 mL of Concd HCl, 100 mL of toluene, and 10 g of the ketonic acid resin (2), preswollen in toluene for 12 h, were added to the zinc amalgam from the above step. The reaction mixture was boiled under reflux for 24 h, cooled, filtered at the pump, washed with water, methanol, chloroform, and acetone, dried in vacuum. Yield 8.59 g;  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$  capacity of the resin, 4.85 meq/g. The band at  $1690\text{ cm}^{-1}$  became weak, but that at  $1450\text{ cm}^{-1}$  still persisted. The absence of any keto group was confirmed from the negative test with the 2,4-dinitrophenylhydrazine reagent.

### **Preparation of Polymeric Butyryl Chloride Resin (4)**

Polymeric butyric acid (3) (7 g) was refluxed with thionyl chloride (40 mL) on a water bath for 3 h until the evolution of HCl vapors ceased. The reaction mixture was cooled and filtered at the pump, washed with chloroform and acetone. Dried in vacuum; yield 7.35 g;  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl}$  capacity of the resin, 4.25 meq/g.

The resin showed an intense absorption band at  $1810\text{ cm}^{-1}$  in the IR spectrum. The presence of chlorine was detected by the Lassaigne's test.

\*The possibility of the formation of a complex between  $\text{AlCl}_3$  and polystyrene [D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**, 9284 (1972)] was eliminated by adding a previously prepared solution of succinic anhydride- $\text{AlCl}_3$  complex to the polystyrene beads.



Chlorine content as determined by the modified Volhard's method was found to be 3.05 meq/g.

### Preparation of 2-Oxopentyl Resin (6)

#### *Preparation of Ethoxy Magnesium Diethyl Malonate*

Magnesium turnings (5.4 g; 0.22 g atom), absolute ethanol (5 mL) and carbon tetrachloride (0.5 mL) were heated on a steam bath. After 15 min, dry ether (50 mL) was added cautiously with stirring. A solution of diethyl malonate (35.2 g, 0.22 mol), ethanol (20 mL, 0.34 mol), and ether (25 mL) was added with stirring at such a rate that rapid boiling was maintained. The mixture was refluxed on a steam bath for 3 h when all magnesium turnings were dissolved.

#### *Preparation of Polymeric Butyryl Malonate (5)*

Polymeric butyryl chloride (6.5 g), preswollen (12 h), was added slowly with stirring to the ethoxy magnesium diethyl malonate from the above step. Heating under reflux was continued until the solution became too viscous to be stirred. The mixture was cooled and shaken with dilute H<sub>2</sub>SO<sub>4</sub> (25 g of concd H<sub>2</sub>SO<sub>4</sub> in 200 mL water). The butyryl malonate resin was collected on a sintered glass filter, washed with water, methanol, chloroform, and acetone and dried. Yield 9.165 g; capacity 3.86 meq/g; IR 1450 cm<sup>-1</sup> (C—O str.), 1650 cm<sup>-1</sup> broad (C=O, ester) (3300 cm<sup>-1</sup> CH str.).

#### *Hydrolysis of Polymeric Butyryl Malonate (5)*

The butyryl malonate resin (8.66 g) was treated with a solution of glacial acetic acid (60 mL), concd H<sub>2</sub>SO<sub>4</sub> (7.6 mL), water (40 mL), and THF (50 mL). The reaction mixture was refluxed for 4 h until the evolution of CO<sub>2</sub> ceased. After cooling, the resin was filtered at the pump, washed with water, ethanol, methanol, and acetone and dried. Yield 6.2 g; capacity 3.12 meq/g; IR 1740 cm<sup>-1</sup> (C=O str.).

### Grignard Reaction of 2-Oxopentyl Resin with MeMgI: Formation of *t*-Alcohol Resin (7)

Methyl iodide (6 mL) was added gradually to a suspension of magnesium turnings (2.5 g) and a crystal of iodine in dry ether (75 mL). When all the magnesium was dissolved, a suspension of preswollen keto resin (6 g) in THF (75 mL) was added to the freshly prepared methyl magnesium iodide with good stirring. The mixture was heated under reflux for 6 h, cooled, filtered, washed with water, methanol, chloroform, and acetone and dried, yield 10.55 g. The resin was heated with dil H<sub>2</sub>SO<sub>4</sub> (20 mL) in THF for 4 h, filtered, washed with THF, methanol, chloroform, and acetone and dried. Yield 6.35 g; capacity 4.01 meq/g. The IR band at 1740 cm<sup>-1</sup> in the original resin disappeared.

### Conversion of the *t*-Alcohol Resin to the Hypochlorite Resin (8)

The *t*-alcohol resin (5 g) preswollen in THF (20 h), was treated with freshly prepared sodium hypochlorite reagent (50 mL, 2M) for 30 h at 30°C. The resin was filtered, washed with water, methanol, chloroform, and acetone and dried. Yield 5.15 g. The resin answered the Lassaigne's test and iodine was evolved when treated with acidified potassium iodide.

ANAL: Cl, 10.06%; 2.84 meq Cl/g.

### Estimation of Chlorine in the Hypochlorite Resin

Two hundred milligrams of the hypochlorite resin was suspended in glacial acetic acid (20 mL) for 20 h; 10 mL of 10% KI and 10 mL of 1N H<sub>2</sub>SO<sub>4</sub> were added. The liberated iodine was titrated against standard thiosulfate using starch as indicator.

### Oxidation of Alcohols with the Hypochlorite Resin (8)

The alcohols (100 mg in the case of solids or 0.4 mL in the case of liquids) were dissolved in chloroform (20 mL) and stirred with a 1.5-fold molar excess of the hypochlorite resin. The reaction was followed by thin-layer chromatography. After the reaction, the resin was filtered and washed with chloroform. The combined filtrate and washings on evaporation of the solvent followed by separation and purification by recrystallization or distillation afforded the corresponding carbonyl compounds. The details of the individual oxidations are given in Table I. The products were identified and characterized by comparison (mp and IR) with authentic specimens.

### Recycling of the Spent Resin

The spent hypochlorite resin (4 g) from the different oxidation reactions was washed successively with THF, methylene chloride, chloroform (20 mL each  $\times$  3 times) filtered and dried *in vacuo*. The dried resin, preswollen in THF (20 h), was treated with a freshly prepared 2M solution of NaOCl reagent in THF as described earlier. The regenerated resin was found to have a capacity of 2.79 meq Cl/g of resin. In the present study, the resin was recycled and reused up to four times for the oxidation of benzoin to benzil.

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