

ing, it seems that lipases from *Candida cylindracea* are the most suitable because they have a higher rate of hydrolysis and higher productivity of fatty acid and are less dependent on temperature. Lipase from *Mucor* is also effective due to excellent pH and temperature characteristics.

The effect of positional specificity in hydrolysis of lipase on the removal of triglyceride soil should be discussed on the basis of examination of the removal of triglyceride and its hydrolysates by surfactant solution. Adaptability of lipase for laundry will be discussed based on the results. This will be reported in the next paper.

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[Received May 1, 1984]

Comparison of Commercially Available Quaternary Ammonium Structures for Phase Transfer Catalysis

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ABSTRACT

A variety of commercially available tetralkyl ($R_1 R_2 R_3 R_4 N^+$) ammonium chlorides and methyl sulfate salts were examined under phase transfer conditions. For conversion of benzyl chloride to benzyl acetate with aqueous potassium acetate, tri C_{8-10} methyl ammonium chloride was the most efficient, with tri C_{16-18} methyl ammonium chloride was next. The alkyl trimethyl ammonium chlorides (particularly C_{12-14} trimethyl) performed well for the oxidation of benzyl alcohol to benzaldehyde with sodium hypochlorite. Trimethyl tallow, C_{16-18} partially unsaturated, ammonium chloride was the catalyst of choice for the dichlorocarbene addition to cyclohexene.

INTRODUCTION

Phase transfer catalysis (PTC) is a rapidly growing field. The industrial applications are limited at present, but most assuredly will increase in the future. One of the earliest applications of phase transfer catalysis by quaternary ammonium salts (quats) is the synthesis of polycarbonates (1). Typically, 2,2-(4,4'-di-hydroxydiphenyl)propane (bisphenol A) is dissolved in concentrated aqueous sodium hydroxide and exposed to a dichloromethane solution of phosgene. Salts such as benzyltriethylammonium chloride or tertiary amines catalyze the condensation polymerization.

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Various linear polymers can be crosslinked with PTC agents also (2). Displacement of halogens by cyanide is common in the manufacture of insecticides (3).

The literature on phase transfer catalysts (4,5) is becoming enormous. However, most PTC work involving quats has centered on:

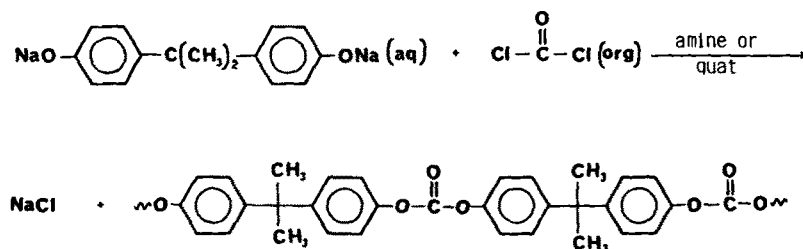
- Examination of one quaternary in one particular reaction on a variety of organic substrates with the same functional group.

- Investigation using one quat in a wide variety of reactions.

A lesser amount of work has occurred on the mechanism of the reactions, solvent choices and effects, and the effect of quat structure. Recent work has involved immobilizing the catalyst on a polymer backbone (6-8).

Certain structures dominate the literature: tetrabutyl ammonium salts, benzyl triethyl ammonium, hexadecyl trimethyl ammonium chloride, or Adogen® 464 (tri C_{8-10} methyl ammonium chloride), and some generalities regarding quat structure have been developed (9-17).

Since certain catalyst structures are more readily available, less expensive and current materials of commerce, we decided to examine various commercially available quaternary ammonium salts (most of which have not been investi-

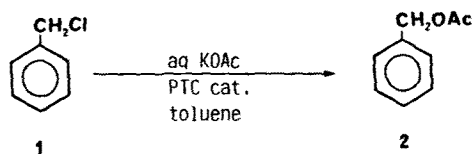


SCHEME 1

QUATERNARIES FOR PHASE TRANSFER

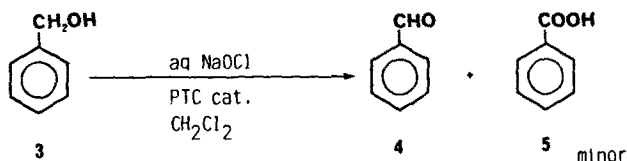
gated or tested) in three illustrative reactions:

- Potassium acetate reaction with benzyl chloride:



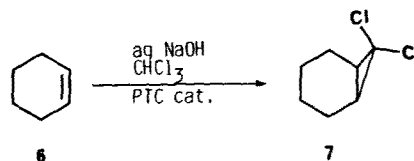
SCHEME 2

- Sodium hypochlorite oxidation of benzyl alcohol to benzaldehyde:



SCHEME 3

- Dichlorocarbene addition to cyclohexene:



SCHEME 4

RESULTS AND DISCUSSION

The reactions were performed under rather mild conditions to differentiate between the catalysts, and thus were not necessarily ideal for highest yields. Since the catalysts are commercially available and sold on a weight basis, they were compared on a weight % basis disregarding their molecular weights differences. Table I reveals the structure of the catalysts along with their efficiency in performing the potassium acetate displacement on benzyl chloride.

TABLE I

Reaction of Potassium Acetate and Benzyl Chloride

Structure no.	Mol. wt. of cation	Catalyst structure	-k ^a	% Benzyl acetate (2)					
				30 min	1 hr	2 hr	4 hr	6 hr	
8	403	(C ₈ H ₁₇ -C ₁₀ H ₂₁) ₃ N [⊕] MeCl [⊖]	.135	11.6	18.0	30.8	45.8	58.3	
9	780	R' ₃ N [⊕] MeCl [⊖]	.107	8.6	14.7	24.2	38.6	49.4	
10	332	Ph-CH ₂ N [⊕] Me ₂ (C ₁₂ H ₂₅ -C ₁₆ H ₃₃)Cl [⊖]	.101	5.4	9.4	17.2	30.9	46.3	
11	403	R' ₂ N [⊕] Me ₂ Cl [⊖]	.094	6.9	12.0	21.0	34.0	44.6	
12	534	R' ₂ N [⊕] Me ₂ Cl [⊖]	.083	7.0	11.0	18.2	32.8	40.4	
13	534	R' ₂ N [⊕] Me ₂ [⊖] OSO ₃ Me	.078	7.9	11.8	17.0	31.1	39.4	
14	243	R''N [⊕] Me ₃ Cl [⊖]	.063	4.7	6.9	14.8	23.7	32.6	
15	303	R'''N [⊕] Me ₃ Cl [⊖]	.063	3.3	8.6	13.0	23.5	32.1	
16	391	R'''Me ₂ N [⊕] (CH ₂) ₃ N [⊕] Me ₃ 2Cl [⊖]	.063	4.0	7.0	12.7	23.2	32.1	
17	242	Bu ₄ N [⊕] Cl [⊖]	.064	2.4	5.4	12.1	21.7	31.4	
18	-	R''MeN [⊕] (CH ₂ CH ₂ O) _x H Cl [⊖] (CH ₂ CH ₂ O) _y H x + y average = 15	.062	4.0	6.6	10.4	22.4	31.4	
19	305	R'N [⊕] Me ₃ Cl [⊖]	.057	5.1	6.4	13.0	21.9	30.1	
20	192	PhCH ₂ N [⊕] Et ₃ Cl [⊖]	.054	2.9	5.4	10.7	19.8	28.0	
21	683		.053	1.5	4.2	9.6	18.5	26.5	
22	200	Bu ₃ N [⊕] MeCl [⊖]	.051	2.1	4.1	10.1	17.8	26.0	
23	620		.048	3.1	5.4	9.9	18.5	25.6	

R' represents the chain lengths present in hydrogenated tallow 33% C₁₆H₃₃, 67% C₁₈H₃₇.
 R'' represents the chain lengths present in coco 9% C₁₀H₂₁, 50% C₁₂H₂₅, 18% C₁₄H₂₉, 11% C₁₆H₃₃, 12% C₁₈H₃₇.
 R''' represents the chain lengths present in unhydrogenated tallow ~33% C₁₆H₃₃, ~18% C₁₈H₃₇, ~49% C₁₈H₃₅.
 R represents the chain lengths present in hydrogenated tallow like R' except one less carbon.

^aPseudo first order rate constant (hr⁻¹) due to an excess of KOAc, average R² = .99.

TABLE II

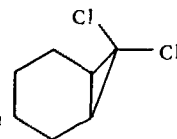
Oxidation of Benzyl Alcohol

Catalyst		30 min	1 hr	2 hr	4 hr
14	benzaldehyde	10.7	29.2	82.7	68.9
	benzyl alcohol	89.3	70.8	4.1	2.8
	unknown (?)	—	—	3.2	2.3
	benzoic acid	—	—	10.0	26.0
15		9.2	34.1	74.2	65.7
		90.8	65.9	9.3	4.4
		—	—	12.6	4.7
		—	—	3.9	25.2
19		13.3	49.7	72.4	65.4
		86.7	50.3	3.0	4.9
		—	—	6.9	3.7
		—	—	17.7	25.8
11		17.1	40.5	74.2	56.2
		82.9	59.5	23.2	15.4
		—	—	.5	8.1
		—	—	2.0	20.3
8		17.5	39.9	74.5	61.5
		82.5	60.1	24.9	19.8
		—	—	.6	1.0
		—	—	.6	17.7
10		15.4	42.9	71.4	60.0
		84.6	56.4	10.4	5.5
		—	.7	11.3	6.9
		—	—	6.8	27.6
17		27.4	45.7	68.3	58.0
		72.6	54.3	25.2	21.8
		—	—	.7	—
		—	—	5.7	20.7
22		16.3	51.7	65.3	57.0
		83.7	48.3	11.8	13.7
		—	—	9.5	.9
		—	—	13.3	28.4
12		16.5	37.9	59.1	56.0
		83.4	62.1	38.0	32.0
		—	—	1.7	—
		—	—	1.2	12.0
9		21.4	43.2	61.1	54.3
		78.6	56.8	36.7	35.9
		—	—	—	—
		—	—	2.2	11.8
13		20.1	35.8	55.0	51.1
		79.9	64.2	43.8	38.2
		—	—	—	—
		—	—	1.2	10.7
16		25.4	38.9	50.5	46.7
		74.6	61.1	49.1	37.4
		—	—	—	6.6
		—	—	.4	9.3
20		12.1	29.1	41.5	43.5
		87.9	70.9	58.5	54.7
		—	—	—	—
		—	—	—	1.8
18		18.0	32.4	31.9	36.6
		82.0	67.6	66.7	62.6
		—	—	1.3	—
		—	—	—	.7
23		3.2	4.6	6.9	15.2
		96.8	95.7	93.1	84.8
		—	—	—	—
		—	—	—	—
21		4.0	6.5	8.4	12.3
		96.0	93.5	91.5	87.7
		—	—	—	—
		—	—	—	—

Since acetate is not a vigorous nucleophile, the temperature and catalyst level were increased to obtain a reasonable reaction rate. Tri C₈₋₁₀ methyl ammonium chloride and tri C₁₆₋₁₈ methyl ammonium chloride performed well, while

TABLE III

Dichloro Carbene Addition



Catalyst	Product						
	-k ^a	15 min	30 min	1 hr	2 hr	3 hr	4 hr
15	.139	11.4	15.1	23.0	33.0	40.7	47.5 ^b
19	.081	10.5	16.0	20.9	25.4	32.3	34.9
22	.071	9.4	12.5	16.0	21.8	26.5	31.2
14	.059	9.9	14.7	18.5	22.6	26.6	29.0
16	.063	8.0	10.5	13.7	19.4	23.5	27.7
18	.067	3.2	7.5	11.0	17.3	21.1	25.8
17	.056	4.3	7.0	10.7	15.1	19.7	22.8
10	.046	5.2	8.7	12.4	16.9	17.2	21.8
20	.044	6.6	8.8	11.3	14.4	18.0	21.6
11	.050	3.7	7.3	10.1	13.6	18.4	20.9
8	.047	5.1	8.5	11.8	16.4	19.7	20.6
9	.053	3.1	5.1	7.9	13.0	17.0	20.7
21	.046	1.0	2.4	5.9	10.5	13.6	16.6
12	.036	3.0	6.5	8.1	11.3	14.7	15.8
13	.022	3.8	8.4	8.7	10.8	11.9	13.3
23	.022	1.4	1.2	3.8	6.2	7.7	8.6

^aPseudo first order rate constant, average R² = .96.

^bIsolated yield of 7 was 35%.

those structures with either fewer or shorter chain lengths were inferior. Apparently, good lipophilicity is needed most. This may indicate the reaction itself is the rate limiting step and not the transfer of acetate ions to the organic phase. The reaction nicely followed pseudo first order kinetics due to the excess of acetate. Certain highly surface active salts did give stubborn emulsions, and this reaction in general compared to the oxidation and carbene addition gave phase separation problems. The rate of reaction seemed to be independent of emulsion formation, indicating these are unrelated phenomena.

Oxidation of benzyl alcohol to benzaldehyde with sodium hypochlorite (Clorox®) occurred easily at room temperature as reported (18). However, the reaction appears somewhat complex.

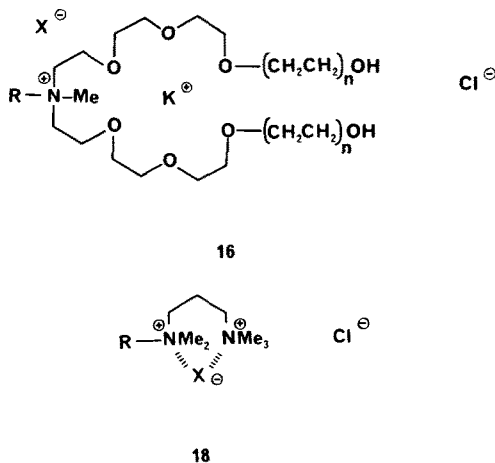
Under the conditions chosen of about 40% excess hypochlorite, some over-oxidation to benzoic acid was observed. There also were small quantities of several materials that were unidentified but appear to be intermediates to benzoic acid. Smooth second order kinetics also were not observed, as some catalysts required an initiation period. This may be the time needed to transfer enough oxidant to the organic phase to accomplish a significant rate of reaction. The most selective catalysts were the alkyl trimethyl salts, particularly the coco (C₁₂₋₁₄ mostly) trimethyl ammonium chloride (Table II). A variety of structures peaked at 70-75% aldehyde. No phase separation problems were observed in this system.

The dichloro carbene addition to cyclohexene to produce 7,7 dichlorobicyclo [4.1.0] heptane was examined under very mild conditions, with tallow trimethyl and hydrogenated tallow trimethyl ammonium chloride being the most effective (Table III). Most of the better structures are strongly surfactant in nature, containing only one long alkyl chain. The data was anticipated to be second order (first order in olefin, first order in caustic, excess of CHCl₃), but under the conditions used it was really pseudo first order in cyclohexene. Again, no phase separation problems existed.

Thus, different structures were demonstrated to be optimal for each reaction. The imidazoline, 23, and amido amine, 21, quats were slightly catalytic though definitely inferior in the three cases tested. The structures are somewhat more complex with additional heteratoms. However,

their ineffectiveness is surprising. No significant difference was detected between the chloride and methyl sulfate salts of the di C₁₆₋₁₈ dimethyl moiety. Structures [8] and [11] are roughly the same molecular weight, with the carbon chains distributed quite differently. Their performance was very similar.

Two compounds [16] and [18] which have potentially strong coordinating power to solubilize reaction ions in the organic phase performed only reasonably well in the carbene reaction. Possibly both are too hydrophilic in nature.



SCHEME 5

Certain catalyst structures may be optimal for selected transformations. However, since a wide variety of compounds can give slightly less than ideal but equivalent results, final catalyst choice for a given reaction may involve weighing several factors, including rate of reaction in a particular solvent system; selectivity; availability and cost; ease of removal and product isolation; ease of recovery or disposal, and toxicity.

EXPERIMENTAL

Catalysts

Benzyl triethyl ammonium chloride was prepared from benzyl chloride and triethyl amine. Tetrabutyl ammonium chloride was made by reacting excess tributyl amine and butyl chloride in isopropyl alcohol at 160 C in a pressure reactor. Purification was via several extractions of CHCl₃/H₂O and CHCl₃/dil HCl to remove olefin by-product, excess amine and amine hydrochloride. After solvent and volatile removal in vacuo, purity was confirmed by C₁₃ NMR.

Tributyl methyl ammonium chloride was obtained from Ethyl Corp. The other catalysts are standard quaternary salts manufactured by Sherex Chemical Co. Most of the quaternaries came as solutions in water and/or isopropyl alcohol. For consistency and convenience, they were used as 50% active solutions by weight in aqueous isopropanol. The concentrations were adjusted to this if necessary.

Analytical

The major portion of the analysis was done on a Varian 3700 gas chromatograph with a thermal conductivity detector and a SP 4000 data station on a 3% Dexil 300 80/100 Gas Chrom Q 4' x 1/8" column. Raw data was corrected for response factors and normalized as needed.

CMR was performed on a Bruker WM-200 NMR spectrometer equipped with an Aspect 2000 data system. All spectra were obtained in pulse mode at a frequency of 50.391 MHz with a simultaneous broadband decoupling of protons at a power of 2 W.

General Procedure

The appropriate reagents were charged to a 500 ml three-necked flask (condenser, thermometer, stirrer - 2 in blade) and brought to the desired temperature. Agitation was vigorous, always using the same stirrer at the same setting. Samples were obtained by momentarily stopping the agitation and pipeting out a small amount of the organic layer.

Acetate Displacement on Benzyl Chloride

A solution of potassium acetate (49.1 g, .5 mol) in water (101 g) was reacted with the organic layer containing benzyl chloride (1, 12.66 g, .1 mol), toluene (120 g), and quat catalyst (1.00 g solution, 4% actual quat by weight of 1) by refluxing at 89 C.

Oxidation of Benzyl Alcohol by Clorox®

Benzyl alcohol (3, 5.04 g, .05 mol), methylene chloride (200 ml), and quat catalyst (.1 g solution, 1% actual quat by weight of 3) were agitated with Clorox® (5.25% NaOCl, 100 g, .07 mol) at 27±3 C (the reactions were started at 24 C, very slowly exothermed to ~30 C, then returned to ~27 C). The slight exotherm was caused by the mixing of the layers, subsequent solvation, etc., and not by the actual chemical reaction.

Dichlorocarbene Addition

Chloroform (90 g, .75 mol), cyclohexene (6, 12.3 g, .15 mol), quat catalyst (.25 g solution, 1% actual quat by weight 6), decalin (4.0 g, GC internal standard), and sodium hydroxide (40% aqueous, 30 g, .30 mol) were reacted with the flask immersed in a water bath at 25 C. Product structure was confirmed by C₁₃ NMR.

ACKNOWLEDGMENT

Ed Fairchild of Sherex Chemical Co. performed the NMR work.

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[Received July 2, 1984]