

shown that β_{nuc} (which, by symmetry, is equivalent to $-\beta_{\text{leaving group}}$)⁷ for this reaction is ~ 0.5 . Because $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{S}^-$ is roughly 10^6 more basic than ES^- , the latter should be a better leaving group in this process by a factor of about 10^3 . It was expected therefore that all measurable nucleophilic attack on the mixed disulfide would occur to give ES^- . The first-order curves generated as shown in Figures 1 and 2 confirm the validity of this assumption.

The greater reactivity of aryl thiol anions compared to alkyl thiol anions of a given basicity may be due to the greater softness of the aryl thiol anions, as discussed previously.¹ It is certainly not due to a favorable interaction between an aryl central thiol and an aryl attacking thiol since changing the central thiol from ES^- to $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{S}^-$ has no effect on the difference in reactivity of the two groups of nucleophiles, as shown in Figure 3.

Limited data exist which allow the inductive effect of the central thiol to be estimated. Shown in Figure 3 is a plot of rate constants for attack of RS^- on ESSE, RSSE, and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SSE}$ plotted as a function of the central thiol $\text{p}K_{\text{a}}$. Only low $\text{p}K_{\text{a}}$ alkyl RSH data were used so that the difference in $\text{p}K_{\text{a}}$ of RSH and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$ would be maximized and the slope generated by the two points would be meaningful. A β_{CT} of approximately -0.3 to -0.4 is found for the inductive effect due to a change in the central thiol. Negative deviations from these lines drawn through the alkyl points were found for the reactions with ES^- as the central thiol. It has previously been demonstrated¹⁸ that the negative charge on ES can cause a fivefold decrease in the rate constant which is consistent with the data in Figure 3.

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Registry No.—ESSE, 552-24-9; 5-[(3-hydroxypropyl)dithio]-2-nitrobenzoic acid, ion(1-), 69531-82-4; 2-nitro-5-[(2,2,3,3,3-pentafluoropropyl)dithio] benzoic acid, ion(1-), 69531-85-3; 2,2,3,3,3-pentafluoropropyl thiolacetate, 69531-84-6; thioacetic acid, 507-09-5; 2,2,3,3,3-pentafluoropropyl iodide, 354-69-8.

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Application of Phase-Transfer Catalysis to the Chemical Modification of Cross-Linked Polystyrene Resins

Jean M. J. Fréchet,* Marc D. de Smet, and M. Jean Farrall

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4, Canada

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The application of phase-transfer catalysis to the introduction of new functionalities in several cross-linked polystyrene resins was studied. In general, the three-phase reactions gave excellent results and high functional yields. Nucleophilic displacements on chloromethylpolystyrene were used to prepare resins containing acetyl, hydroxymethyl, cyanomethyl, dinitrile, mononitrile monoester, diester, thiol, and various other functionalities. Addition of cyanide ion to a polystyrylcarboxaldehyde resin produced cyanohydrins which could be trapped by reaction with acetic anhydride or a reactive halide. Other phase-transfer reactions involving the use of thiol, hydroxyl, or cyanomethyl resins as nucleophiles were also studied. Reactions involving symmetrical difunctional molecules occurred mostly at one extremity only, indicating that in these phase-transfer reactions site-site interactions can be limited.

The preparation of polymers carrying various functional groups is a problem which has received much attention in recent years, as evidenced by the large body of literature devoted to this subject.^{1,2} Functional polymers have been used in a large variety of applications in which they may serve as supports, reagents, or catalysts for various reactions.³ The polymers which are used most often in these applications are cross-linked polystyrene resins. These are chosen mainly because the aromatic rings of the polymer can be functionalized relatively easily while the polymer itself has good mechanical and chemical resistance.¹ One of the most important reactions in the functionalization of cross-linked polystyrene is doubtless its chloromethylation⁴ since the chloromethyl group provides a reactive handle on the polymer and can

subsequently be transformed into numerous other functional groups.¹ Two other important steps in the functionalization of cross-linked polystyrene, bromination and lithiation, have been described in a previous report from this laboratory,⁵ and a number of functional polymers have been prepared from lithiated polystyrene.^{1,5,6}

A large number of reactions can be used to effect the chemical modification of polymers but in a number of cases the reactions are accompanied by undesired side reactions and the functional yields are low. Since the functional polymers cannot be purified once they have been prepared, it is desirable to use very simple systems in the functionalization reactions to avoid all side reactions whenever possible.

For the past year we have been using phase-transfer catal-

Table I. Reaction of $\text{P-CH}_2\text{Cl}$ with Nucleophiles under Phase-Transfer Conditions

starting resin	mequiv/g	DF	swelling agent ^a	catalyst	reagent	temp, °C	time, days	structure of product	product anal., mequiv/g			product DF	functional yield, % ^b
									Cl	N	Other		
	1.8	0.205	A	Adogen 464	CH_3COOK	100	4	$\text{P-CH}_2\text{OCOCH}_3$	0		1.70 (ester)	0.200	98
	1.8	0.205	A	$(\text{Bu})_4\text{NCl}$	CH_3COOK	100	4	$\text{P-CH}_2\text{OCOCH}_3$	0		1.70 (ester)	0.200	98
	1.8	0.205	B	Adogen 464	CH_3COOK	80	4	$\text{P-CH}_2\text{OCOCH}_3$	0.08		1.66 (ester)	0.198	96 (100)
	1.8	0.205	C	Adogen 464	CH_3COOK	25	4	$\text{P-CH}_2\text{OCOCH}_3$	1.03				43 (100)
	2.1	0.24	D	$(\text{Bu})_4\text{NOH}$	$\text{CH}_3(\text{CH}_2)_3\text{SH}$, NaOH	65	2	$\text{P-CH}_2\text{S-}(\text{CH}_2)_3\text{CH}_3$	0		1.92 (S)	0.24	100
	2.1	0.24	A	$(\text{Bu})_4\text{NOH}$	$\text{CH}_3(\text{CH}_2)_3\text{SH}$, NaOH	65	2	$\text{P-CH}_2\text{S-}(\text{CH}_2)_3\text{CH}_3$	0		1.90 (S)	0.24	100
	2.1	0.24	D	$(\text{Bu})_4\text{NOH}$	$\text{HS}(\text{CH}_2)_4\text{SH}$, NaOH	25	1	$\text{P-CH}_2\text{S-}(\text{CH}_2)_4\text{SH}$	0		3.50 (S)	0.23	95
	1.8	0.205	B	Adogen 464	NaCN	80	4	$\text{P-CH}_2\text{CN}$	trace	1.84		0.205	100
	2.6	0.310	C	Adogen 464	NaCN	25	3	$\text{P-CH}_2\text{CN}$	0.4	2.3		0.250	81 (100)
	1.8	0.205	A	$(\text{Bu})_4\text{NOH}$	$\text{HOPh-}p\text{-CHO}$, KOH	80	3	$\text{P-CH}_2\text{OPh-}p\text{-CHO}$	0		3.06 (O)	0.200	98
	1.8	0.205	A	$(\text{Bu})_4\text{NOH}$	$\text{HOPh-}p\text{-NO}_2$, KOH	85	2	$\text{P-CH}_2\text{OPh-}p\text{-NO}_2$	0	1.52	4.47 (O)	0.203	99
	1.8	0.205	A	Adogen 464	$\text{CH}_2(\text{CN})_2$, KOH	90	5	$\text{P-CH}_2(\text{CN})_2$	trace	3.3		0.200	98
	1.8	0.205	A	Adogen 464	$\text{CH}_2(\text{COOEt})_2$, KOH	90	5	$\text{P-CH}_2\text{-CH}(\text{COOEt})_2$	0.10		4.8 (O)	0.158	77 (81)
	1.8	0.205	A	Adogen 464	$\text{CH}_2(\text{CN})\text{COOEt}$, KOH	90	5	$\text{P-CH}_2\text{-CH}(\text{CN})\text{COOEt}$	0.09	1.4	2.76 (O)	0.181	88 (92)

^a A = *o*-dichlorobenzene; B = 1,2-dichloroethane; C = dichloromethane; D = benzene. ^b % sion given in parentheses.

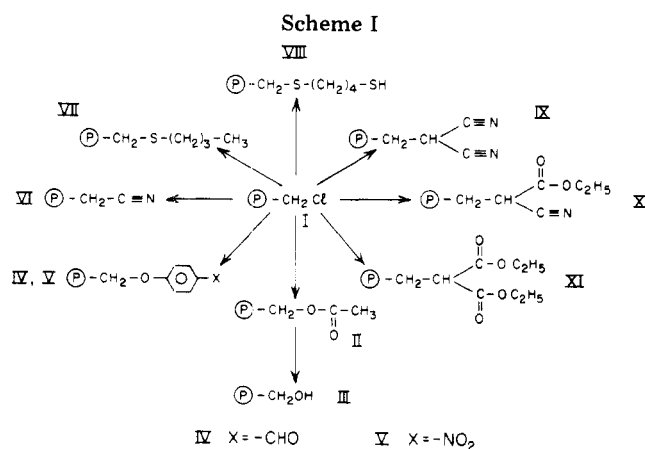
ysis for the generation of reactive intermediates on insoluble polymers; for example, polymer supported sulfur ylids have been used in the preparation of epoxides from carbonyl compounds.⁷ Reactions involving such three-phase systems were found to be generally quite slow but proceeded in remarkably clean fashion with excellent yields and without appreciable formation of side products.

This manuscript describes the use of phase-transfer catalysis⁸ in the three-phase preparation of reactive insoluble polymers starting from resins carrying chloromethyl,⁴ aldehyde,^{5,9,10} thiol,^{5,6} hydroxyl,⁶ or cyanomethyl¹⁰ groups. In two instances reactions involving symmetrical bifunctional reagents were studied and an evaluation of site-site interactions was made.

Results and Discussion

A. Nucleophilic Substitutions on Functional Polymers.

The reaction of nucleophiles with chloromethylated polystyrene I (Scheme I) has long been used to prepare resins containing new functionalities.¹ We have carried out a number of nucleophilic substitutions on resin I using a variety of C,



S, or O nucleophiles using a three-phase system consisting of two liquid phases, organic swelling agent and aqueous solution of the nucleophile, and a solid resin in the presence of a phase-transfer catalyst.

The first reaction we studied was the replacement of chloride with acetate, a reaction which had been carried out successfully as early as 1965 by Ayres and Mann¹⁰ using potassium acetate in dimethyl sulfoxide. However, our experience with reactions involving I in dimethyl sulfoxide indicates that these are always accompanied by some oxidation to the aldehyde. As can be seen in Table I, the reaction with a concentrated aqueous solution of potassium acetate under phase-transfer conditions was successful but did not result in complete displacement of chloride when carried out at room temperature in dichloromethane. In contrast, essentially complete conversion was obtained when the reaction was carried out at a higher temperature using *o*-dichlorobenzene or 1,2-dichloroethane using either tetrabutylammonium chloride or Adogen 464 as phase-transfer catalyst. In a typical reaction the starting polymer, which contained 1.80 mequiv of chlorine/g for a degree of functionalization (DF) of 0.205, was transformed cleanly into the acetylated polymer II which had no remaining chlorine. The infrared spectrum of II had large absorption bands at 1750 and 1235 cm^{-1} characteristic of C=O and C—O absorptions, respectively. Saponification of polymer II with excess base followed by back titration with acid indicated that the polymer contained 1.70 mequiv of acetyl groups/g for a degree of functionalization of 0.201 indicating that the phase-transfer catalyzed reaction was essentially quantitative. Conversion of II into the hydroxymethylated polymer III was carried out easily using aqueous sodium or potassium hydroxide and tetrabutylammonium hydroxide or Adogen 464 as catalyst. Again the reaction was complete as evidenced by the absence of carbonyl absorption in the infrared spectrum of III.

Similar displacements using oxygen nucleophiles derived from *p*-hydroxybenzaldehyde and *p*-nitrophenol under phase-transfer conditions with aqueous sodium hydroxide

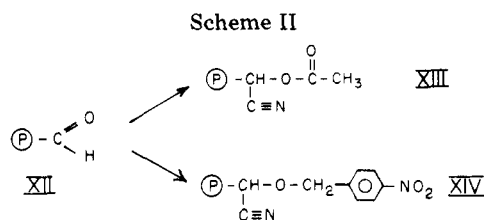
gave the expected products IV and V in essentially quantitative yields. Polymer IV had characteristic infrared absorptions at 2755, 1695, and 1150 cm^{-1} . The same polymer has also been prepared in excellent yield by Gibson and Bailey using a classical route.² Polymer V had absorptions for the nitro group at 1345 and 855 cm^{-1} and C—O absorptions at 1165 and 1005 cm^{-1} . In both cases no appreciable amount of chlorine could be detected in the polymer.

The preparation of cyanomethyl polystyrene from I has also been described by Ayres and Mann¹⁰ who used potassium cyanide in Me_2SO for the reaction. However, as was the case earlier for the reaction with potassium acetate, the reaction also produced some aldehyde by oxidation of the chloromethyl groups. We have carried out this displacement in quantitative yield using sodium cyanide in dimethylformamide at 80 °C. Alternatively, this reaction can be carried out in almost quantitative yield using I with aqueous sodium cyanide under phase-transfer conditions. The polymeric nitrile VI which is obtained has a very sharp CN absorption band in its infrared spectrum at 2260 cm^{-1} . Both the reaction in dimethylformamide and the phase-transfer reaction produce a reactive cyanomethylated polymer free from aldehyde contamination.

The polymeric sulfide (VII) was obtained in quantitative yield by the reaction of butanethiol with I in the presence of hydroxide ion with tetrabutylammonium hydroxide as catalyst. Both benzene and *o*-dichlorobenzene were found to be satisfactory in this reaction. A similar reaction with methanethiol also gave a quantitative yield of the corresponding sulfide. The reaction with a difunctional molecule such as 1,4-butanedithiol was also studied although complications such as the formation of additional cross-links through reaction at both extremities of the dithiol could be expected. Indeed, when the reaction is carried out in a two-phase system using polymer I and a solution of 1,4-butanedithiol in dimethylformamide containing base, extensive site interactions are observed¹¹ even under conditions in which a large excess of the dithiol is used. In contrast, when the reaction is carried out under phase-transfer conditions to limit the concentration of thiolate in the polymer phase, double coupling can be reduced drastically and polymer VIII can be obtained with a functional yield of 95%.

The reaction of resin I with various C nucleophiles obtained from malononitrile, ethyl cyanomalonate, and diethyl malonate, in the presence of aqueous sodium hydroxide and Adogen 464 as phase-transfer catalyst, also produced some valuable results. The dinitrile resin IX was obtained in essentially quantitative yield and had a very sharp CN absorption band at 2200 cm^{-1} in its infrared spectrum. A similar resin has been prepared recently by Gaudemer and co-workers¹² using a solution of malononitrile in dimethylformamide with alkoxide as base. This reaction produced polymer IX in 30% yield only. With ethyl cyanomalonate and diethyl malonate the phase-transfer-catalyzed reaction produced the mononitrile monoester resin X and the diester resin XI in satisfactory functional yields of 88 and 77%, respectively. In these two cases, the final polymer still contained a small but measurable amount of chlorine. It is however interesting to note that in both of these reactions no hydrolysis of ester was observed as confirmed by the infrared spectra of X and XI which did not exhibit any absorption band corresponding to a carboxylic acid but had strong ester bands at 1745 and 1740 cm^{-1} . A somewhat similar polymer has been prepared very recently in 90% yield by Pittman and Kim¹³ using polymer I and the anion of diethyl 2-methylmalonate using 5:1 benzene-ethanol as solvent.

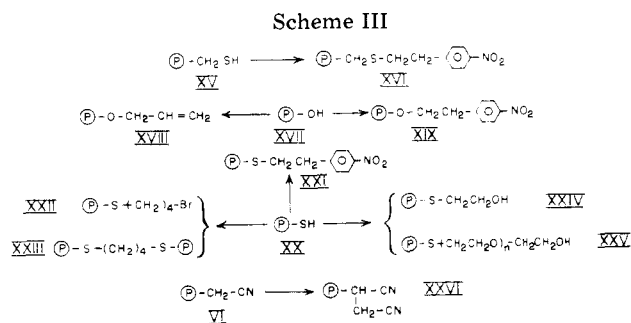
B. Nucleophilic Addition of CN^- to $\text{P}-\text{CHO}$. The phase-transfer-catalyzed addition of cyanide (Scheme II) to polymeric aldehyde XII^{1,5} was tested using conditions under



which the intermediate cyanohydrin would be trapped to yield a cyanohydrin acetate (XIII) or a cyanohydrin ether (XIV). Unlike the substitution reactions described above which were best carried out at 70–80 °C for several days, the addition of cyanide to XII in the presence of acetic anhydride to form XIII could be carried out at room temperature in a relatively short time. Since it was expected that acetic anhydride would be hydrolyzed rapidly by the very alkaline aqueous solution of sodium cyanide, addition of acetic anhydride was effected very slowly over the course of the reaction. The reaction was accompanied by the complete disappearance of the aldehydic C—H and C=O absorptions and their replacement by a very strong ester band at 1755 cm^{-1} in the IR spectrum. Similarly, when the addition was carried out in the presence of *p*-nitrobenzyl bromide as trapping agent, new bands due to the nitro group appeared in the infrared spectrum replacing the aldehydic bands. By reaction with a polymeric aldehyde XII containing 3.6 mequiv of functional group/g (DF = 0.42) a resin XIV containing 4.04 mequiv of nitrogen/g was obtained (DF = 0.34) for a functional yield of 81%.

C. Reactions Involving Polymeric Nucleophiles. The use of $\text{P}-\text{CH}_2\text{SH}$ as a polymeric nucleophile under phase-transfer conditions was studied in the displacement of bromide from *p*-nitrophenethyl bromide, a reaction which yields polymer XVI (Scheme III) which can be characterized easily by elemental analysis. Since the method of preparation of XV⁶ affords a polymer in which all the sulfur is present as thiol, provided extreme care is exercised to prevent formation of disulfides, it is expected that the reaction of the thiolate of XV with *p*-nitrophenethyl bromide will be complete and yield a product, XVI, which will contain equivalent amounts of sulfur and nitrogen. The reaction, carried out under phase-transfer conditions with exclusion of atmospheric oxygen, gave an excellent result with formation of a product which contained 1.58 mequiv of sulfur and 1.58 mequiv of nitrogen/g of XVI. The same reaction carried out in the presence of atmospheric oxygen gave extensive disulfide formation. Similarly, polymer XVII⁶ can generate the polymeric phenolate which, by reaction with *p*-nitrophenethyl bromide under phase-transfer conditions, gave XIX in close to 90% functional yield. The reaction with allyl bromide under phase-transfer conditions also gave a product in which no hydroxyl remained as evidenced by the IR spectrum of XVIII. Attempts to characterize XVIII by bromination of its double bond to yield the dibromide were inconclusive as the final product contained more bromine than expected, probably due to some allylic bromination.

Another interesting phase-transfer reaction involving the



use of a polymer nucleophile is the displacement of bromide from a symmetrical molecule such as 1,4-dibromobutane using the anion of polystyrylmercaptan XX.⁶ Such a reaction is somewhat more complex than the previous one as two different products XXII and XXIII can be obtained. Polymer XXII would be obtained exclusively if the reaction sites of XX behaved as if they were completely isolated from one another resulting in a reaction only at one end of 1,4-dibromobutane; in this case, the product XXII would contain as many bromine atoms as there were reactive thiolate ends on XX. In contrast, if the thiolate end groups can react at each of the extremities of 1,4-dibromobutane, the final product will contain an appreciable amount of XXIII as well as XXII and thus the number of bromine atoms in the final product (XXII + XXIII) will be lower than the number of reactive thiolate groups which took part in the reaction. Therefore, a simple evaluation of the amount of double coupling in this reaction can be obtained from a measurement of the number of reactive ends in polymer XX and from analytical data on the bromine and sulfur content of the product of the reaction of the anion of XX with 1,4-dibromobutane.

The number of reactive end groups in P-SH was determined by reaction with *p*-nitrophenethyl bromide under phase-transfer conditions, a reaction which was shown to proceed to completion in the case of polymeric thiol XV in which all sulfur atoms are reactive. An earlier study of polymer XX had indicated that only a fraction of the sulfur in the polymer was present as thiol.⁶ This observation was confirmed by the results of the reaction of XX with *p*-nitrophenethyl bromide which gave XXI. In a typical reaction the final product (XXI) contained 1.37 mequiv of nitrogen and 1.88 mequiv of sulfur/g which indicated that approximately 27% of the sulfur in XX is unreactive. The reaction of XX with 1,4-dibromobutane can be compared directly to the reaction with *p*-nitrophenethyl bromide since in both reactions the same amount of sulfur on XX is unreactive and both products XXI and XXII have essentially the same functional group molecular weights. Therefore one would expect that should XX react with only one end of 1,4-dibromobutane, the resulting polymer would contain 1.37 mequiv of bromine/g. In fact, the reactions gave a product containing only 1.23 mequiv of Br/g indicating that the reaction gave approximately 10% double coupling. Obviously these results can only be deemed to be accurate within $\pm 5\%$.

The reaction of XX with 2-chloroethanol under phase-transfer conditions is also a reaction which can lead to more than one product, XXIV and XXV, since the alcohol which is formed initially can react with more 2-chloroethanol in a Williamson type synthesis. Our result in this experiment confirms this expectation as the final product of the reaction usually contains more oxygen than there was reactive sulfur in the starting polymer. XXIV can however be prepared more satisfactorily under classical two-phase conditions by formation of the polymeric thiolate, followed by removal of excess base and addition of 2-chloroethanol. It should be noted however that a long-chain polyether derived from XXV may find useful applications.

A final phase-transfer reaction involving a polymeric nucleophile was carried out with the *p*-cyanomethylated polystyrene VI which by reaction with chloroacetonitrile gave the dinitrile XXVI in approximately 90% yield. The dinitrile polymer had an infrared spectrum which showed two sharp CN bands at 2200 and 2250 cm^{-1} . Reaction of the dinitrile with more chloroacetonitrile in the presence of hydroxide under phase-transfer conditions failed to yield the polymeric trinitrile which would form should the abstraction of both acidic hydrogens of the starting polymer be possible. The lack of reactivity of the second hydrogen is probably due to a steric problem.

Experimental Section

The styrene-divinylbenzene resins used in this investigation were a 1% cross-linked solvent swellable copolymer (Bio-beads SX1, Bio-Rad Laboratories) and a 2% cross-linked macroreticular copolymer (Amberlite XE 305). All the phase-transfer catalysts which were used can be purchased from Aldrich Chemical Co. Reagents and solvents were reagent grade and used without further purification. Infrared spectra were recorded on a Pye-Unicam SP 1100 infrared spectrophotometer using potassium bromide pellets. Elemental analyses were carried out by MHW laboratories (Phoenix, Ariz.) with duplicate analyses by Galbraith laboratories or this laboratory.

Washing of the Resins. All the resins used in this project were washed routinely to remove surface impurities using a procedure described earlier.⁵ All the solvents used in these and other washings of the resins were recycled after use. Trace elemental analyses confirmed the purity of the polymers: C, 92.18; H, 7.69; total halogen, 0.09; N, none; S, none; O, none.

Preparation of $\text{P-CH}_2\text{Cl}$. The procedure used for this reaction was a modification of that of Pepper et al.⁴ In a typical reaction, 70 g of Amberlite XE-305 was suspended into a mixture of 520 mL of chloroform and 140 mL of chloromethyl ethyl ether. The suspension was stirred mechanically for 1 h at room temperature and 14 mL of anhydrous stannic chloride was added dropwise with stirring. A gradual change in color, white to yellow, was observed. After completing the addition of stannic chloride, an additional 70 mL of chloromethyl ethyl ether was added and the reaction was allowed to proceed for 2 h and 40 min with constant stirring. The resin was then collected on filter and washed extensively with methanol, chloroform, dioxane-water 3:1, dioxane-3 N HCl 3:1, dioxane, dioxane-water 3:1, water, and finally methanol. After drying under vacuum at 50 °C, the polymer weighed 81.9 g and contained 3.00 mequiv of Cl/g (DF = 0.365).

A similar procedure carried out on 49.5 g of Bio-beads SX1, swollen in 250 mL of chloroform and 100 mL of chloromethyl methyl ether, with 2 h of stirring prior to cooling to 0 °C and addition of 6 mL of stannic chloride in 80 mL of chloromethyl methyl ether with 30 min of stirring at 0 °C and 1 h of stirring at 25 °C gave 54.2 g of a polymer containing 1.80 mequiv of Cl/g (DF = 0.205).

Preparation of $\text{P-CH}_2\text{CN}$. A suspension of 30 g of $\text{P-CH}_2\text{Cl}$ (2.43 mequiv/g) and 9 g of NaCN in 250 mL of dimethylformamide was stirred at 75–80 °C for 4 h. The mixture was filtered and the polymer washed with water, methanol, water, dioxane-water 4:1, DMF, dioxane, acetone, chloroform, and finally methanol. After drying under vacuum overnight at 80 °C, 28.66 g of polymer was obtained. The polymer had a sharp CN band in its infrared spectrum at 2280 cm^{-1} and contained 3.35% N or 2.4 mequiv of CN/g.

Phase-Transfer Reactions on $\text{P-CH}_2\text{Cl}$ (Table I, Scheme I).
Preparation of II. To 0.969 g of $\text{P-CH}_2\text{Cl}$ (SX1, 1.8 mequiv/g) in 8 mL of *o*-dichlorobenzene were added 0.3 g of Adogen 464 and 3 g of potassium acetate in 5 mL of water. The mixture was placed in an oil bath at 100 °C and stirred magnetically for 4 days. After filtration the polymer was washed repeatedly with methanol, water, THF-H₂O 3:1, THF, acetone, dichloromethane, and methanol. After drying overnight at 60 °C under vacuum, the polymer weighed 1.006 g and its infrared spectrum had large bands at 1750 and 1235 cm^{-1} . The saponification equivalent of II was determined by treating the polymer with an excess of aqueous potassium hydroxide in a heterogeneous mixture consisting of ca. 0.5 g of polymer with 5 mL of aqueous KOH and 15 mL of THF with 0.05 g of tetrabutylammonium hydroxide at 75 °C for 24 h. After back titrating with 0.1 N HCl, it was determined that the polymer contained 1.70 mequiv of ester/g. See analytical data in Table I.

Preparation of IV. The reaction was carried out as for II using 1 g of $\text{P-CH}_2\text{Cl}$, 15 mL of *o*-dichlorobenzene, 5 g of *p*-hydroxybenzaldehyde, 0.1 mL of a 40% solution of tetrabutylammonium hydroxide, and 2.3 g of KOH in 5 mL of H₂O. The final polymer had an infrared spectrum with bands at 2755 (aldehydic CH), 1695 (C=O), and 1150 cm^{-1} .

Preparation of V. The reaction involved 1 g of $\text{P-CH}_2\text{Cl}$ with 15 mL of *o*-dichlorobenzene, 0.1 mL of a 40% solution of tetrabutylammonium hydroxide, 6 g of *p*-nitrophenol, and 4.2 g of KOH in 11 mL of H₂O. Infrared spectrum: bands at 1345 and 855 (NO₂) and 1165, 1005 cm^{-1} (C—O).

Preparation of VI. The reaction involved 1 g of $\text{P-CH}_2\text{Cl}$ with 8 mL of 1,2-dichloroethane, 0.2 g of Adogen 464, and 3 g of NaCN in 7 mL of H₂O. Infrared spectrum: 2280 cm^{-1} (CN). A control experiment carried out under the same conditions but without phase-transfer catalyst resulted in the removal of only 26% of the chlorine from $\text{P-CH}_2\text{Cl}$ after 4 days at 80 °C.

Table II. Phase-Transfer Reactions on Miscellaneous Polymers

starting resin no.	mequiv/ g		swell- ing ^a agent	catalyst ^b	reagent	temp, °C	time, days	structure of product	product anal. mequiv/g			prod- uct DF	func- tional yield, %
	DF								N	S	Other		
II	1.70	0.20	A	(Bu) ₄ NOH	KOH	85	2	Ⓟ-CH ₂ OH				0.20 ^c	100
XII	3.60	0.42	B	TEBAC	KCN,(CH ₃ CO) ₂ O	70	1.5	Ⓟ-CH(CN)OCOCH ₃	2.42			0.33	79
XII	3.60	0.42	B	TEBAC	KCN,BrCH ₂ Ph- <i>p</i> - NO ₂	45	1.5	Ⓟ-CH(CN)OCH ₂ Ph- <i>p</i> -NO ₂	4.04			0.34	81
XV	2.04	0.24	A	Adogen 464	BrCH ₂ CH ₂ Ph- <i>p</i> - NO ₂ , NaOH	75	2	Ⓟ-CH ₂ SCH ₂ CH ₂ Ph- <i>p</i> -NO ₂	1.58	1.58		0.24	100
XVII	2.18	0.235	A	(Bu) ₄ NOH	BrCH ₂ CH ₂ Ph- <i>p</i> - NO ₂ , NaOH	50	3	Ⓟ-OCH ₂ CH ₂ Ph- <i>p</i> - NO ₂	1.51			0.209	89
XVII	2.18	0.235	A	Adogen 464	BrCH ₂ CH=CH ₂ , NaOH	65	3	Ⓟ-O-CH ₂ CH=CH ₂					
XX	2.50	0.28	D	(Bu) ₄ NI	BrCH ₂ CH ₂ Ph- <i>p</i> - NO ₂ , NaOH	25	1	Ⓟ-SCH ₂ CH ₂ Ph- <i>p</i> - NO ₂	1.37	1.86			
XX	2.50	0.28	D	(Bu) ₄ NI	Br(CH ₂) ₄ Br	25	1	Ⓟ-S(CH ₂) ₄ Br			1.23 (Br)		
XX	2.12	0.235	D	(Bu) ₄ NOH	ClCH ₂ CH ₂ OH, NaOH	65	1.2	Ⓟ-S(CH ₂ CH ₂ O) _{<i>n</i>} - CH ₂ CH ₂ OH	1.7	2.3 (O)			
VI	2.50	0.29	A	Adogen 464	ClCH ₂ CN, NaOH	25	4	Ⓟ-CH(CH ₂ CN)CN	2.06			0.26	88

^a A = *o*-dichlorobenzene; B = 1,2-dichloroethane; D = benzene. ^b TEBAC = triethylbenzylammonium chloride. ^c Calculated from saponification and esterification experiments.

Preparation of VII. The reaction involved 1.5 g of Ⓟ-CH₂Cl in 15 mL of benzene, 0.1 mL of a 40% solution of tetrabutylammonium hydroxide, 5 mL of butanethiol, and 1.5 g of NaOH in 5 mL of H₂O. The reaction was carried out under a nitrogen atmosphere.

Preparation of VIII. The reaction involved 1.4 g of Ⓟ-CH₂Cl in 15 mL of benzene, 0.13 g of a 40% solution of tetrabutylammonium hydroxide, 6 mL of 1,4-butanedithiol, and 0.8 g of NaOH in 6 mL of H₂O. The reaction was carried out under a nitrogen atmosphere.

Preparation of IX. The reaction involved 1 g of Ⓟ-CH₂Cl in 11 mL of *o*-dichlorobenzene, 0.2 g of Adogen 464, 3 g of malononitrile, and 2.5 g of KOH in 6 mL of H₂O. Infrared spectrum: 2200 cm⁻¹ (CN).

Preparation of X. The reaction involved 1 g of Ⓟ-CH₂Cl in 7 mL of *o*-dichlorobenzene, 0.4 g of Adogen 464, 3 g of ethyl cyanoacetate, and 3 g of KOH in 5 mL of H₂O. Infrared spectrum: 2220, 1750 cm⁻¹.

Preparation of XI. The reaction involved 1 g of Ⓟ-CH₂Cl in 10 mL of *o*-dichlorobenzene, 0.4 g of Adogen 464, 3 g of diethyl malonate, and 3 g of KOH in 6 mL of H₂O. Infrared spectrum: 1745 cm⁻¹ (COOEt).

Preparation of Ⓟ-CH₂OH (III). The reaction was carried out on 2 g of polymer II prepared above swollen in 14 mL of *o*-dichlorobenzene with 0.25 mL of 40% tetrabutylammonium hydroxide solution and 5 g of KOH in 5 mL of H₂O. The final product had an infrared spectrum which contained no carbonyl absorption and hydroxyl bands at 3460 and 3635 cm⁻¹.

Ⓟ-CH₂OH can also be prepared directly from Ⓟ-CH₂Cl using 1.1 g of I (1.8 mequiv/g) swollen in 10 mL of *o*-dichlorobenzene with 0.3 g of 40% tetrabutylammonium hydroxide solution, 3 g of potassium acetate, and 2 g of KOH in 6 mL of H₂O. The mixture is stirred at 85 °C for 2 days then filtered and washed to yield the desired hydroxymethyl polymer.

Phase-Transfer-Catalyzed Additions to Ⓟ-CHO (Table II, Scheme II). **Preparation of XIII.** The reaction was carried out on 1 g of Ⓟ-CHO (3.60 mequiv/g) swollen in 12 mL of 1,2-dichloroethane with 0.1 g of triethylbenzylammonium chloride and 3 g of KCN in 4 mL of H₂O. The stirred mixture was heated to 70 °C and 4 mL of acetic anhydride were added dropwise over a 24-h period. After 1.5 days the mixture was filtered and washed as for II. The infrared spectrum of XIII included a small band at 2230 cm⁻¹ and a large band at 1770 cm⁻¹.

Preparation of XIV. The reaction was carried out as above replacing the slow addition of acetic anhydride with a slow addition of *p*-nitrobenzyl bromide at 45 °C.

Phase-Transfer Reactions with Polymer Nucleophiles (Table II, Scheme III). **Preparation of XVI.** The reaction was carried out with 0.83 g of Ⓟ-CH₂SH in 15 mL of *o*-dichlorobenzene with 0.4 g of Adogen 464, 3 g of *p*-nitrophenethyl bromide, and 2 g of NaOH in 3 mL of H₂O under inert atmosphere. After filtration the polymer was washed as above to yield 1.07 g of XVI with no SH band and NO₂

bands at 1345 and 1520 cm⁻¹ in the infrared spectrum.

Preparation of XVIII. The reaction involved 1 g of Ⓟ-OH in 10 mL of *o*-dichlorobenzene with 0.2 g of Adogen 464 and 2.1 g of KOH in 5 mL of H₂O. Allyl bromide (2.0 mL) was added dropwise over 24 h to the stirred reaction mixture. The infrared spectrum of the product showed no remaining hydroxyl.

Preparation of XIX. The reaction involved 1 g of Ⓟ-OH in 12 mL of *o*-dichlorobenzene with 0.2 g of Adogen 464 and 2 g of KOH in 5 mL of H₂O. *p*-Nitrophenethyl bromide, 2 g, was added in small portions over 24 h. The infrared spectrum of XIX had no OH absorptions but contained NO₂ bands at 1345 and 1520 cm⁻¹.

Preparation of XXI. The reaction involved 1 g of Ⓟ-SH in 15 mL of benzene, 0.081 g of tetrabutylammonium iodide, and 1 g of NaOH in 2 mL of H₂O with 2 g of *p*-nitrophenethyl bromide under inert nitrogen atmosphere. Infrared spectrum: NO₂ bands at 1345 and 1520 cm⁻¹.

Preparation of XXII + XXIII. The reaction involved 1 g of Ⓟ-SH in 15 mL of benzene, 0.081 g of tetrabutylammonium iodide, and 1 g of NaOH in 2 mL of H₂O with 2 mL of 1,4-dibromobutane under inert nitrogen atmosphere.

Preparation of XXIV + XXV. The reaction involved 1 g of Ⓟ-SH in 10 mL of benzene, 0.12 mL of tetrabutylammonium hydroxide solution (40%), and 3 g of NaOH in 5 mL of H₂O with 1 mL of 2-chloroethanol. Infrared spectrum: large hydroxyl at 3460 and 3640 cm⁻¹.

Preparation of XXVI. The reaction involved 1 g of Ⓟ-CH₂CN in 8 mL of *o*-dichlorobenzene, 0.12 mL of a 40% tetrabutylammonium hydroxide solution, and 2.5 g of NaOH in 5 mL of water with slow addition of 1 mL of 2-chloroacetonitrile over 2 days. Infrared spectrum: two CN bands at 2200 and 2250 cm⁻¹. The same reaction carried out in dichloromethane at room temperature gave exactly the same result.

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Synthesis and Reaction of Substituted Arylalkoxyiodinanes: Formation of Stable Bromoarylalkoxy and Aryldialkoxy Heterocyclic Derivatives of Tricoordinate Organoiodine(III)

Ronald L. Amey and J. C. Martin*

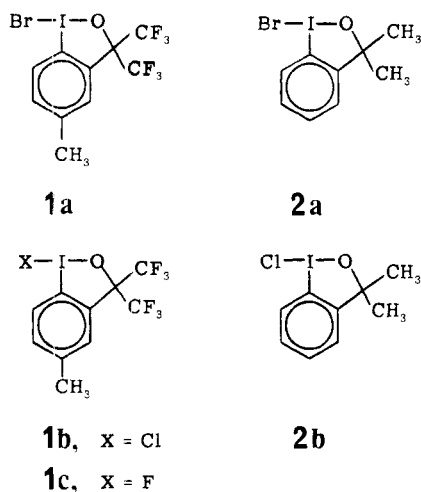
Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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The first stable, crystalline bromoiodinanes, **1a** and **2a**, as well as the first aryldialkoxyiodinanes, have been synthesized from the respective alcohols **4** and **5**. Two chloroiodinanes, **1b** and **2b**, have been prepared by chlorination of the parent alcohols. Bromo- and chloroiodinanes have been shown to be synthetically useful as highly selective, free-radical halogenating agents for benzylic and allylic hydrogens. Reactivity patterns of these species differ sufficiently from those evidenced by other iodine(III) species, to suggest a possible niche for these compounds in synthetic organic chemistry. Treatment of either **1b** or **2b** with potassium hexafluoroantimonate (KOR_F) gives the respective dialkoxy species **8** or **9**. Degenerate ligand exchange for either **8** or **9** occurs rapidly on the NMR time scale with 0.08-0.10 M KOR_F ($T_8 = 56^\circ\text{C}$, $T_9 = 93^\circ\text{C}$), but not with a comparable concentration of R_FOH , suggesting an associative exchange mechanism.

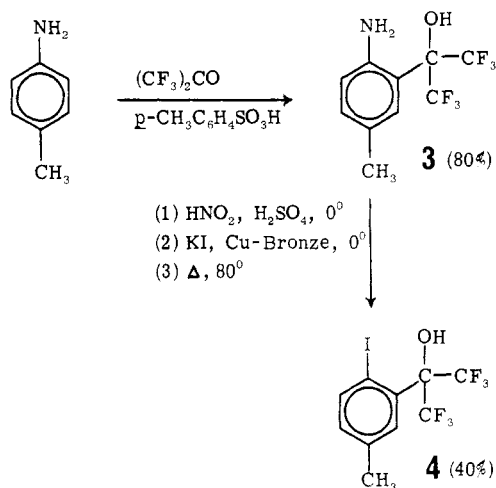
Stable bromoiodinanes have never been isolated, although both chloro and fluoro analogues have been known for over 40 years.¹ The preparation of phenyliodine dibromide was reported in 1905,² but the compound was not isolated nor characterized, and subsequent attempts at its synthesis in these laboratories have failed. There are no reports of the isolation of inorganic analogues such as IBr_3 , although the possible existence of the latter in solution³ and as a complex with theobromine⁴ has been discussed.

We report here the details of the synthesis of two stable isolable bromoiodinanes, **1a** and **2a**, as well as chloro and fluoro analogues, **1b-c** and **2b**.



Our success in isolating the stable bromoiodinanes **1a** and **2a** is attributed to the stabilizing influence of the five-membered ring and, in the case of **1a**, to the highly electronegative trifluoromethyl substituents. The trifluoromethyl-substituted species are markedly more stable than their simple methyl analogues.

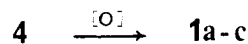
Scheme I



Results

The trifluoromethyl-substituted alcohol **4**, the key intermediate in the synthesis of iodinanes **1a-c**, is readily prepared by the method of Scheme I. This utilizes the known⁵ reaction of hexafluoroacetone with *p*-toluidine, in the presence of a suitable catalyst, to introduce the perfluoroalkyl groups.

Treatment of **4** with suitable oxidizing agents results in the formation of the stable, crystalline iodinanes **1a-c**. In the



- 1a**, $[\text{O}] = (1) \text{KH}$, (2) Br_2 (90%)
1b, $[\text{O}] = \text{tert-BuOCl}$ or Cl_2 (96%)
1c, $[\text{O}] = \text{CF}_3\text{OF}$ (95%)

preparation of **1c**, care must be taken to avoid excess trifluoromethyl hypofluorite as further oxidative fluorination of **1c** to the iodine(V), periodinane, species occurs.⁶ Compound **1c**