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Preparation of Alkyl Chlorides, Acid Chlorides, and Amides Using Polymer-Supported Phosphines and Carbon Tetrachloride: Mechanism of These Reactions

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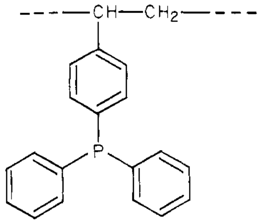
Alcohols and thiols were converted into alkyl chlorides, carboxylic acids were converted into acid chlorides, and mixtures of carboxylic acids and amines were converted into amides by reaction with carbon tetrachloride and 1% cross-linked polystyrenes containing phosphine residues. Some of these conversions were also effected by using a linear polymer containing phosphine residues. The reactions proceed in high yield, and isolation of the products is facilitated by the ready removal of all the polymer-supported species. The mechanism of the reactions between triphenylphosphine, carbon tetrachloride, and alcohols is complex, but the polymer-supported reactions appear to follow analogous pathways to the low molecular weight reactions as judged by the yields of chloroform and the number of equivalents of phosphine consumed per mole of alkyl chloride produced. The mechanism requires polymer-supported groups reacting together. The slow step in the reactions appears to be the generation of the chlorinating species. The polymer-supported reactions are faster than those using triphenylphosphine or 4-(diphenylphosphinyl)isopropylbenzene. It is suggested that this is due to a microenvironmental effect.

The triphenylphosphine–carbon tetrachloride reagent can be used for various chlorination, condensation, and dehydration reactions.[1,2] It is an attractive reagent in that conditions are mild and yields are generally high, but separation of the products from the phosphorus-containing byproducts can present difficulties,[3] especially with small-scale reactions. We describe here our work on the polymer-supported phosphine (1)–carbon tetrachloride reagent. This reagent can be used to convert alcohols[4] or thiols[5] into alkyl chlorides and acids into acid chlorides[6] or amides.[7] It has the attractive feature that all the phosphorus-containing byproducts can be removed at the end of the reaction simply by filtering off the polymer.[8] The supported reactions appear to proceed by mechanisms similar to those operating with the triphenylphosphine–carbon tetrachloride reagent, but the supported reactions are faster, possibly due to a microenvironmental effect. Since we initiated this work,[9] other workers have reported some studies of the same reagent.[10–12] Their results are considered where appropriate in the ensuing discussion.

Results and Discussion

Preparation of the Polymers. Linear and cross-linked polymers containing phosphine residues (1) were prepared by brominating[13] the appropriate polystyrenes and then treating the products with chlorodiphenylphosphine and lithium.[14] As this procedure is widely used, two observations we have made are noteworthy. First, not all the bromo groups that react in the phosphination reaction are replaced by diphenylphosphinyl groups; some are simply reduced. This suggests that a halogen–metal exchange reaction occurs and that some of the residues **2** so produced survive until the reaction is quenched with methanol. Second, the phosphination reaction tends to degrade the polymer. Thus, the weight of the cross-linked products were often substantially less than expected, and a typical linear product had a molecular weight of 90 000 instead of 250 000 as expected. The cross-linked products were nevertheless quite stable in the subsequent work. The linear polymers were also satisfactory except that on prolonged storage they tended to cross-link and become insoluble.



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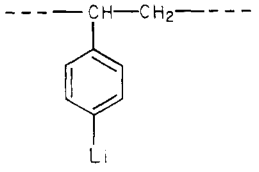

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The phosphine contents of the polymers were estimated by elemental analysis for phosphorus. As some workers have claimed such analyses to be high and variable,[10,14] the phosphorus contents of several cross-linked polymers were also estimated by reaction with *n*-hexyl bromide or benzyl bromide. These reactions can be carried out in high yield,

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Table I. Conversion of Octan-1-ol into 1-Chlorooctane with Phosphine Resin and Carbon Tetrachloride in Various Solvents[a]

	reaction conditions			
solvent	temp, °C	time, h	yield of chloride,[b] %	recovd alcohol,[b] %
CCl_4	77	1	99	
	60	3	72	14
	40	16	40	
$ClCH_2CH_2Cl$[c]	80	1	99	
	60	3	94	0
CH_2Cl_2[c]	40	3	87	
	40	6	93	
$CHCl_3$[c]	60	3	45	34
CH_3CN[c]	60	3	21	53
THF	60	3	15	6
C_6H_6[c]	60	3	7	71

[a] Reactions used 2.5 mmol of 1% cross-linked polystyrene containing 2.39 mmol of phosphine/g, 1.0 mmol of octan-1-ol, and 10 mL of solvent. [b] By GLC analysis. [c] Solvents contained 10% by volume of carbon tetrachloride.

Table II. Conversion of Alcohols and Thiols into Alkyl Chlorides by Treatment with Phosphine Polymers (2 Equiv) in Carbon Tetrachloride[a]

substrate	polymer[b]	reaction time, h	yield of chloride,[c] %
octan-1-ol	X	1.5	98[d,e]
	L	2	93[d]
hexadecan-1-ol	X	2	98[f]
octadecan-1-ol	L	2	76
3-phenylpropan-1-ol	X	2	98[f]
	L	3	95[d]
4,4,4-triphenylbutan-1-ol	X	3	94
5β-cholan-24-ol	X	2.5	98[g]
2-*n*-butoxyethanol	X	1	94[d]
4-(hydroxymethyl)-2,2-dimethyldioxolane	X	6	78[d]
cinnamyl alcohol	X	4	100[f]
benzyl alcohol	X	1	77[f]
	L	2	91[d]
p-chlorobenzyl alcohol	X	3	100
octan-2-ol	X	3	76[d,h]
cyclohexanol	X	5	40[d,i]
octadecanethiol	X	3	78[f]
3-phenylpropanethiol	X	2	82[d]
phenylmethanethiol	X	2	95[d]
	L	2	91[d]

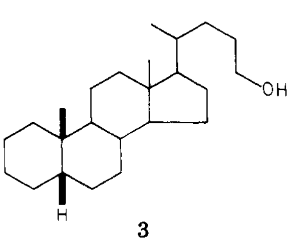
[a] Unless indicated otherwise the reactions were carried out at reflux temperature. [b] X = 1% cross-linked polymer with 2.50 mmol of phosphine/g. L = linear polymer with 2.69 mmol of phosphine/g. [c] Unless indicated otherwise recoveries were >90% and the remaining material was the alcohol or thiol. [d] By GLC analysis. [e] From a preparative-scale reaction 1-chlorooctane was isolated in 76% yield. [f] Chloride isolated as a liquid with spectroscopic data (IR, ^1H NMR) identical with those of an authentic sample. [g] 78% yield after recrystallization. See the Experimental Section. [h] A mixture of octenes formed in 8% yield. [i] Cyclohexene formed in 50% yield.

and the phosphonium salt contents of the products can be estimated from the substantial gain in weight of the polymers and by halide ion titrations. In most, but not all, cases the results were in satisfactory agreement, and we conclude that while occasional elemental analyses were high, in general they were satisfactory. Unless indicated otherwise, the reactions discussed below were carried out by using 1% cross-linked polymers containing 1.2–2.5 mmol of phosphine/g or linear polymers containing 2.7–3.0 mmol of phosphine/g.

Preparation of Alkyl Chlorides. With reagents prepared from lightly cross-linked polymers the choice of reaction solvent is particularly important,[8,15] since it must swell the polymer throughout the reaction in order that the substrate molecules can gain access to the reactive groups. Preliminary experiments (see Table I) showed that the present reagent reacted satisfactorily with octan-1-ol in carbon tetrachloride, 1,2-dichloroethane, or methylene dichloride.

A range of alcohols and two thiols were treated with the supported phosphine 1 in carbon tetrachloride under reflux (see Table II). Excellent yields of alkyl chlorides were obtained from the primary alcohols and benzyl alcohols, from cinnamyl alcohol, and from the two thiols. With secondary alcohols some elimination occurred, and mixtures of chloride and olefin were obtained. Other workers have carried out similar reactions but the range and variety of substrates studied was much smaller than that in Table II.[10,11]

Because substrates need to diffuse into polymer-supported reagents to react, such reagents can be expected to show some substrate selectivity based on size.[16-19] 5β-Cholan-24-ol (3) and 4,4,4-triphenylbutan-1-ol are relatively large substrates, but they both reacted satisfactorily with the present reagent. Indeed, when an equimolar mixture of octan-1-ol and 4,4,4-triphenylbutan-1-ol was treated with a deficiency of the supported reagent, the yields of the corresponding chlorides were 55% and 45%, respectively. From a similar reaction using the phosphine 4 in place of the polymer the corresponding yields were 48% and 52%. These results suggest that with the present reagent the rate of diffusion of the substrate into the polymer is not a major factor in determining the reaction rate.



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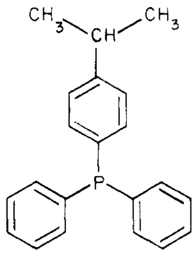

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Polymer-supported reagents are not often prepared from linear (soluble) polymers because in most cases the spent polymers are not easily separated from the other reaction products.[20] However, linear polymers were satisfactory in the present case (see Table II). The starting polymers were soluble in carbon tetrachloride but became insoluble as the reactions proceeded, and at the end of the reaction period they could be filtered off without difficulty.

Preparation of Acid Chlorides and Amides. Various carboxylic acids were converted into acid chlorides by using the 1% cross-linked polymers in carbon tetrachlorides (see Table III). In each case the polymer was filtered off at the end of the reaction period and an infrared spectrum

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Table III. Conversion of Acids into Acid Chlorides by Treatment with Phosphine Resin[a] (2 Equiv) in Carbon Tetrachloride under Reflux for 4 h

acid	yield of deriv, %	deriv	recovd acid, %
n-octanoic	63	amide	7
phenylacetic	50	*p*-toluidide	
stearic	82	amide	13
phenoxyacetic	50	anilide	5
	60[b]	anilide	3
3-*O*-acetyl-lithocholic acid	82[c]	methyl ester	13[d]
cinnamic	77	*p*-toluidide	5
benzoic	90	*p*-toluidide	3
β-naphthoic	84	methyl ester	11
α-furoic	82	*p*-toluidide	8

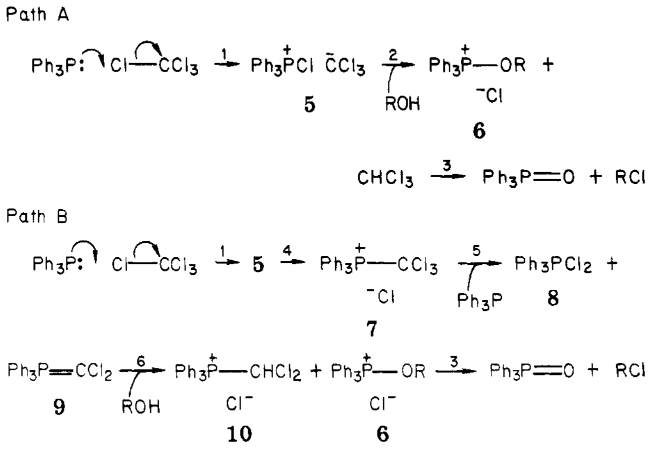
[a] 1% cross-linked polymer containing 2.50 mmol of phosphine/g. [b] The solvent was 1,2-dichloroethane containing 10% of carbon tetrachloride. [c] 3 equiv of phosphine used. [d] Not isolated. The figure given is the total recovery less the yield of the ester.

Table IV. Preparation of Amides by Reaction of Acids and Amines with Phosphine Resin and Carbon Tetrachloride[a]

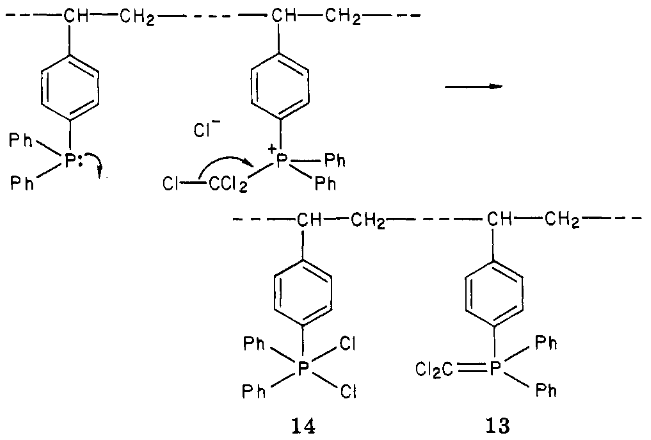
acid	amine	reaction solvent[b]	yield of amide,[c] %
stearic	aniline	DCE	86
phenoxyacetic	aniline	CCl_4	57
		DCE	72
cinnamic	*p*-toluidine	CCl_4	83
benzoic	*p*-toluidine	CCl_4	94
biphenyl-4-carboxylic	aniline	DCE	73

[a] Reactions used 2.0 mmol of 1% cross-linked polystyrene containing 2.50 mmol of phosphine/g, 1.0 mmol of acid, 2.2 mmol of amine, and 20 mL of solvent. Reaction mixtures were heated under reflux for 3 h. [b] DCE = 1,2-dichloroethane containing 10% by volume of carbon tetrachloride. [c] Yield of crystalline solid with a satisfactory melting point.

Scheme I



Scheme II[a]



[a] Compare with reaction 5 in Scheme I.

of the filtrate measured prior to treatment of the latter with an alcohol or amine to give a solid derivative. Some acid was always recovered, and judging from the infrared spectra of the initial products in most cases this was due largely to the formation of anhydride. Reactions using triphenylphosphine in place of the polymer generally gave similar yields of anhydrides.

Acids can be converted into amides more directly and efficiently by treatment with the supported reagent in the presence of at least 2 molar equiv of the amine.[7] Our results are summarized in Table IV. Appel and Willms have recently prepared several peptides in this manner.[12]

Mechanism of the Reactions. It is well-known that the triphenylphosphine–carbon tetrachloride reagent converts alcohols into alkyl chlorides by two pathways (see Scheme I).[1,2,21] We considered it of interest to see whether the polymer-supported reactions proceeded similarly because this would require two supported residues reacting together as shown in Scheme II.

In pathway A, triphenylphosphine reacts with carbon tetrachloride to give intermediate **5**.[22] This reacts with the alcohol to give chloroform and the alkoxyphosphonium salt **6**, which then decomposes to give the alkyl chloride and phosphine oxide. The overall reaction is, therefore, as summarized in eq 1.

$$ROH + Ph_3P + CCl_4 \rightarrow RCl + Ph_3P{=}O + CHCl_3 \tag{1}$$

$$ROH + 2Ph_3P + CCl_4 \rightarrow RCl + Ph_3P{=}O + \underset{\mathbf{10}}{Ph_3P^+\text{-}CHCl_2\ Cl^-} \tag{2}$$

$$2ROH + 3Ph_3P + CCl_4 \rightarrow 2RCl + 2Ph_3P{=}O + \underset{\mathbf{11}}{Ph_3P^+\text{-}CH_2Cl\ Cl^-} \tag{3}$$

The first step in pathway B is also the formation of intermediate **5**, but in this case it rearranges to the (trichloromethyl)phosphonium salt **7**, and the latter then reacts with more triphenylphosphine to give triphenylphosphine dichloride (**8**) and dichloromethylene ylide (**9**). These now react with the alcohol to give the alkoxyphosphonium salt **6**, which reacts further as before, and the (dichloromethyl)phosphonium salt **10**. The reaction may end here, or the latter may react in a similar cycle of reactions to give the (chloromethyl)phosphonium salt **11**.[21] The overall reaction in pathway B is, therefore, as summarized in eq 2 or 3, depending on whether salt **10** reacts further.

The relative contributions of pathways A and B (for simplicity, the reactions in Scheme I are also taken to represent the analogous polymer-supported reactions) for the reactions of triphenylphosphine and various polymers with carbon tetrachloride and octan-1-ol were estimated by measuring the number of moles of chloroform formed and the number of moles of phosphine consumed per mole of 1-chlorooctane produced (see Table V). When one

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(21) Tömöskoözi, I.; Gruber, L.; Radics, L. *Tetrahedron Lett.* **1975**, 2437.

(22) Appel[1,2] considers that the initial product is best described as the "dipolar associate", $Ph_3P^{\delta+}\cdots Cl\cdots{}^{\delta-}CCl_3$.

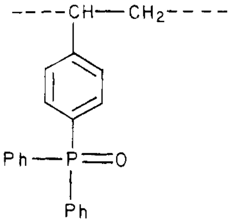
Table V. Reaction of Various Phosphines with Carbon Tetrachloride and Octan-1-ol: Yields of Chloroform and Consumption of Phosphine Relative to the Yields of 1-Chlorooctane[a]

phosphine or type of polymer	mmol of phosphine/g	mmol of $CHCl_3$ formed/mmol of 1-chlorooctane		mmol of phosphine used/mmol of 1-chlorooctane
		actual	corr[b]	
triphenylphosphine	3.81	0.23	0.21	1.70
linear polystyrene	2.69	0.39	0.29	1.69
	3.00	0.36	0.27	1.84
1% cross-linked polystyrene	1.25			2.50
	2.39	0.40	0.27	2.10
	3.16			2.05
	3.40	0.31	0.18	2.00
2% cross-linked polystyrene	2.15	0.33	0.22	1.92
20% cross-linked macroporous polystyrene	1.13			7.40

[a] Reactions used 2.0 mmol of phosphine and 1.5 mmol of octan-1-ol in 10 mL of CCl_4. The mixture was vigorously stirred and heated under reflux for 6 h. [b] Reaction of triphenylphosphine with carbon tetrachloride in the absence of a substrate produced 0.01 mmol of $CHCl_3$/mmol of phosphine used. In the presence of linear or cross-linked polystyrene the production of chloroform doubled. Reaction of linear or cross-linked polystyrene containing phosphine residue 1 with carbon tetrachloride in the absence of a substrate produced 0.06 mmol of $CHCl_3$/mmol of phosphine used. Reaction of cross-linked polymer or triphenylphosphine with carbon tetrachloride in the absence of substrate but in the presence of 2.0 mmol of chloroform resulted in the recovery of >90% of the chloroform.

allows for the chloroform produced when the phosphines reacted with carbon tetrachloride in the absence of octan-1-ol (see Table V, footnote *b*),[23] the results from the various reactions were very similar. They indicate that in all cases pathway A only accounted for 18–29% of the 1-chlorooctane produced and that pathway B was the major route.

Further support for pathway B being the major route in the polymer reactions was obtained by showing (i) that the spent linear polymer contained 0.8 chlorine atoms per phosphorus atom and was soluble in methanol whereas linear polymer containing only phosphine oxide residues 12 (prepared by oxidation of the starting polymer[14]) was insoluble in methanol, (ii) that treatment of the spent cross-linked polymers with trichlorosilane and triethylamine, a reagent which reduces phosphine oxide residues 12 back to phosphine residues 1,[24] only regenerated about 40% of the original activity, and (iii) that the dichloromethylene ylide 13, formed by reacting the polymer with carbon tetrachloride in the absence of octan-1-ol, reacted with benzaldehyde to give *β,β*-dichlorostyrene (60% of the maximum yield expected if the phosphines reacted entirely as in Scheme II).[25]



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We conclude, therefore, that the polymer-supported reactions follow pathways analogous to those of the reactions using triphenylphosphine and that in both systems the 1-chlorooctane is produced mainly by pathway B or its polymeric analogue. The latter involves two polymer-supported residues reacting together as shown in Scheme II. The chlorides formed from other sterically unhindered primary alcohols are almost certainly produced similarly.

It is interesting to note that the 20% cross-linked macroporous polymer afforded a much smaller yield of 1-chlorooctane per millimole of phosphine than the other polymers we studied (see Table V). Similar results were obtained by Sherrington and his co-workers, who prepared various macroporous polymers containing phosphine residues and studied their reactions with carbon tetrachloride and octan-1-ol or hexadecan-1-ol.[11] It appears that with the relatively inflexible highly cross-linked macroporous polymers the reaction shown in Scheme II, and therefore pathway B, is severely restricted. It is interesting to note that in these circumstances, pathway A does *not* efficiently produce 1-chlorooctane. This result, not readily obtained without the use of polymers, suggests that the relative contributions of the two pathways are usually determined by the relative rates of reactions 2 and 4 (see Scheme I). With more acidic substrates than alcohols the analogue of reaction 2 would be expected to be faster and pathway A to play a bigger part.[11]

The reactions of octan-1-ol, three other sterically unhindered primary alcohols, and two carboxylic acids were investigated further. In these cases the yields of alkyl or acyl chlorides obtained after various times from reactions using polymer-supported phosphines in carbon tetrachloride were compared with those from analogous reactions using the same number of millimoles of triphenylphosphine or phosphine 4, a better model for the polymer, in the same volume of solvent. In some cases reactions were carried out at 40 or 60 °C to make them easier to follow. The results are summarized in Table VI, and typical progress curves are shown in Figures 1 and 2. Detailed analysis of such data for polymer-supported reactions is generally very difficult because as the reactions proceed the microenvironment in the vicinity of the reaction sites alters due, for example, to changes in the swelling properties of the polymer and to differences in the polarity of the original residues and the reacted residues. In the present case there is the added complication with the supported reactions that the curves are S shaped. It is nevertheless clear from Figures 1 and 2 that for a given substrate the initial reaction rates depend on the phosphine used and decrease in the order cross-linked polymer > linear polymer > phosphine 4 > triphenylphosphine and from Table VI that for a given substrate the yields of

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[23] It is not clear why chloroform is produced in small amounts from triphenylphosphine and CCl_4 in the absence of an alcohol, but it probably arises as the result of an electrophilic species, for example, 5 or 8, attacking a phenyl residue. Consistent with this, the production of chloroform increases when polystyrene is added, and it increases still further when the phosphine moiety is part of the polymer.

[24] Heitz, W.; Michels, R. *Justus Liebigs Ann. Chem.* **1973**, 227.

[25] Rabinowitz, R.; Marcus, R. *J. Am. Chem. Soc.* **1962**, *84*, 1312.

Table VI. Reaction of Phosphines with Various Substrates in Carbon Tetrachloride: Yields after Various Reaction Times[a]

		reaction conditions		technique used to monitor reaction[c]	% yield			
							1	
substrate	concn[b]	temp, °C	time		Ph_3P	4	L	1% XL
octan-1-ol	C	77	30 min	G	3[f]			97
	C	60	2 h	G	4[d]	15[d]	30[f]	50[d]
	D	60	2 h	G	2			28
	C	40	4 h	G	2	4	19	33
3-phenylpropan-1-ol	C	40	4 h	H			16[e]	42[e]
n-butoxyethanol	C	77	30 min	G	4			75
benzyl alcohol	C	60	2 h	G	4[g]	32[f]	60[f]	76[f]
	C	40	4 h	H			26[e]	62[e]
	D	40	4 h	H			18	45
octanoic acid	C	77	30 min	I	3	15[f]		44[f]
benzoic acid	C	77	30 min	I		20[f]		63[f]
	D	77	30 min	I		12		46

[a] Reactions generally used 1.0 mmol of substrate and 2.0 mmol of phosphine. [b] C = reactions carried out with 10 mL of CCl_4. D = reactions carried out with 30 mL of CCl_4. [c] G = GLC; H = HPLC; I = intensities of carbonyl bands in the infrared spectrum. [d] See Figure 1. [e] See Figure 2. [f] The yields of products were >90% after 24 h. [g] The yields of product were >90% after 4 days.

Table VII. Conversion of Octan-1-ol into 1-Chlorooctane Using Phosphines and Hexachloroethane[a]

		reaction conditions		% yield	
phosphine	solvent	temp, °C	time, h	chloride	$Cl_2C{=}CCl_2$
triphenylphosphine	CH_2Cl_2	40	4	100	100
	CCl_4	40	4	56	56
	CCl_4	40	0.5	50[c]	
1% cross-linked polymer[b]	CH_2Cl_2	40	4	60	57
	CCl_4	78	2	80	76
	CCl_4	40	0.5	20[d]	

[a] Reactions used 1.2 mmol of phosphine, 1.1 mmol of C_2Cl_6, and 1.0 mmol of octan-1-ol in 10 mL of solvent. Yields were determined by GLC. [b] Contained 1.25 mmol of phosphine/g. [c] Under similar conditions but in the absence of C_2Cl_6 the yield was 2% after 0.5 h and >80% after 4 days. [d] Under similar conditions but in the absence of C_2Cl_6 the yield was 3% after 0.5 h and >85% after 4 days.

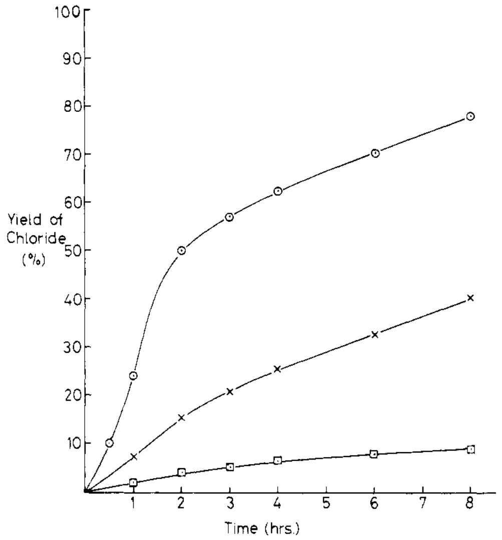


Figure 1. Conversion of octan-1-ol into 1-chlorooctane by using 1.0 mmol of substrate and 2.0 mmol of various phosphines in 10 mL of CCl_4 at 60 °C: □, Ph_3P; ×, phosphine 4; ○, cross-linked polymer.

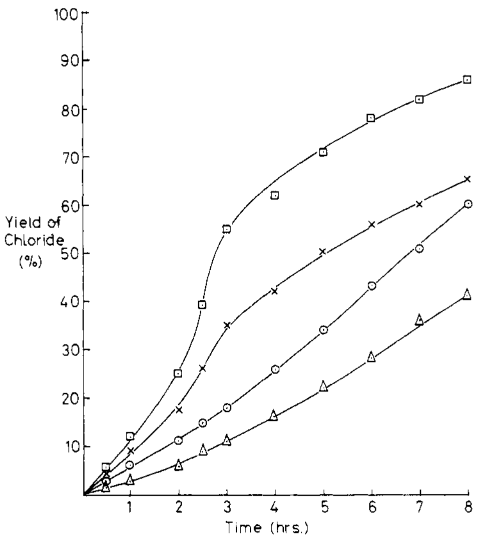
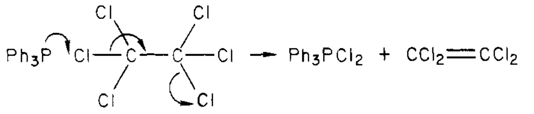


Figure 2. Conversion of benzyl alcohol and 3-phenylpropanol to the corresponding chlorides by using 1.0 mmol of substrate and 2.0 mmol of phosphine polymer in 10 mL of CCl_4 at 40 °C: △, 3-phenylpropanol with linear polymer; ○, benzyl alcohol with linear polymer; ×, 3-phenylpropanol with cross-linked polymer; □, benzyl alcohol with cross-linked polymer.

product obtained in a given time decrease in the same order.

Clearly, to some extent the polymer-supported reactions are faster than those using triphenylphosphine because the supported phosphines are actually alkyl-substituted triphenylphosphines, but to understand why the polymer-supported reactions are faster than those using phosphine 4 it is necessary to identify the slow steps in these reactions. As noted above, in the reactions of octan-1-ol using the 1% cross-linked polymer or triphenylphosphine at least 70% of the 1-chlorooctane was produced by pathway B. To determine whether the slow step on this pathway was one involved in the formation of the chlorinating species [8 or the supported analogue 14 (see Scheme II)] or a subsequent reaction, we generated these intermediates by a different route, and their reactivities were compared with the phosphine–carbon tetrachloride reagents.

Reaction of the phosphines with hexachloroethane in the presence of the substrate proved to be a suitable method (see reaction 7 and Table VII).[26] Comparison of the


(7)

yields of 1-chlorooctane obtained by treating octan-1-ol and triphenylphosphine with hexachloroethane in carbon tetrachloride at 40 °C and with neat carbon tetrachloride at 40 °C showed that the former reaction was considerably faster (50% and 2% yields of 1-chloro-octane, respectively, after 0.5 h; see the footnotes of Table VII for details of yields over longer reaction periods). Similar results were obtained by using the 1% cross-linked polymer in place of the triphenylphosphine (20% and 3% yields, respectively, after 0.5 h; see the footnotes of Table VII for details of yields over longer reaction periods). The triarylphosphine dichlorides may actually react with the octan-1-ol more rapidly than these results suggest, because in the reactions with hexachloroethane the generation of **8** and **14** may be the slow processes. We conclude that in each of the reactions using the phosphine–carbon tetrachloride reagents, the slow process in the production of alkyl chlorides from unhindered primary alcohols is the generation of the chlorinating species. This result agrees with that of Franzus et al., who studied the reactions of triphenylphosphine and carbon tetrachloride with alcohols.[27]

The rate of the reaction between triphenylphosphine and carbon tetrachloride is known to be very sensitive to the choice of reaction solvent, and it has been concluded that polar substrates can act as solvating agents and assist the reaction.[28] We suggest that the polymer-supported reactions are faster than those using phosphine **4** because the reactions produce phosphonium salts (see Scheme I) and that while with the nonpolymeric reagents these can disperse throughout the reaction medium, with the cross-linked polymers they cannot, and they create within the polymer a favorable microenvironment for the initial reaction. This microenvironment is also likely to attract the polar substrate molecules into the polymer and so assist the initial reaction even further. Indeed, Sherrington has observed that alcohol molecules show a preference for the spent polymer rather than the solution.[11] These effects would also explain why the rate curves are S shaped: the rates increase initially as the number of polar groups on the polymers accumulate. With the linear polymers the effects are likely to be smaller because they are better able than the cross-linked polymers to expand to minimize electrostatic interactions and hence to reduce the polarity of the microenvironment. Other workers have attributed differences between supported and nonsupported reagents to microenvironmental effects.[29]

Experimental Section

The 1% and 2% cross-linked polystyrenes were, respectively, Biobeads SX1 and SX2 (Bio-Rad, Richmond, CA) in the form of 200–400-mesh beads. The 20% cross-linked polystyrene was Biobeads SM-2 in the form of 20–50-mesh beads. The linear polystyrene was obtained from RAPRA, Shawbury, Great Britian. Polymers were filtered off by using No. 4 grade sintered-glass filters and were dried in a vacuum oven (0.1 mmHg) at 50 °C to constant weight. Molecular weights ($\bar{M}_n$) were determined with a Knauer membrane osmometer with toluene as the solvent at 37 °C. Elemental analyses were carried out by Butterworths Microanalytical Laboratories, Teddington, Middlesex, England, or by Dr. A. M. G. Macdonald, Chemistry Department, University of Birmingham, Great Britian. The degree of functionalization (DF) is the fraction of the phenyl residues of the polystyrene which bears the functionality in question. GLC was carried out with a Pye 104 machine (flame-ionization detector) with a 5 ft column containing either PEGA or SE-30 as the stationary phase. HPLC was carried out with a Waters machine (UV detector set at 254 nm) with 25 cm × 4 mm columns containing Partisil-10 PAC and hexane or hexane–chloroform (9:1) as the eluent. In both these chromatographic techniques peak areas were determined by triangulation, and authentic samples were used to identify peaks and determine the response ratios. Melting points were determined with a Kofler hot-stage apparatus. ^{1}H NMR spectra were recorded at 60 MHz for ca. 10% solutions in deuteriochloroform containing tetramethylsilane as an internal reference.

Cross-Linked Polymers with Phosphine Residues 1. The cross-linked polystyrenes were brominated by using bromine and thallic acetate hydrate in CCl_4 according to the procedure of Farrall and Frěchet.[13] The products were reacted with Li and diphenylphosphinous chloride in THF by using the procedure of Relles and Schluenz.[14]

In a typical phosphination reaction brominated 1% cross-linked polystyrene (36.92 g, DF = 0.80) gave a product (27.68 g) which by elemental analyses contained 2.39 mmol of residues 1/g (DF = 0.45) and 0.03 mmol of bromo groups/g. (DF = 0.01). For a product of this composition the expected weight of polymer was 41.09 g. Anal. Found: P, 7.20, 7.60; Br, 0.25.

Reaction of the above product (2.000 g) with neat benzyl bromide (10 mL) at 90 °C for 3 h, followed by thorough washing of the polymer with CH_2Cl_2 gave, after drying, the phosphonium salt (2.757 g). Volhard titrations[30] using 200-mg samples of polymer and ferric alum as the indicator showed the product contained 1.55 mmol of bromide ion/g. The gain in weight of the polymer and the bromide ion determination respectively indicate that the starting polymer contained a *minimum* of 2.21 and 2.14 mmol of phosphine residues 1/g.

Linear Polymers with Phosphine Residues 1. The linear polystyrene used had, by our experiments, $\bar{M}_n$ = 130 000.

This was brominated by using a modification of the method of Farrall and Frěchet for cross-linking polystyrenes.[13] In a typical bromination, Br_2 (12.8 g) in CCl_4 (10 mL) was added dropwise over 1 h to a solution of polystyrene (10.4 g) and thallic acetate sesquihydrate (614 mg) in CCl_4 (150 mL) at 20 °C. After the addition was complete, the mixture was heated under reflux for 2 h. It was then cooled and added to MeOH (2 L). The precipitate was collected, dissolved in $PhCH_3$ (200 mL), and reprecipitated into MeOH (2 L). The precipitate was collected and dried to give the product (15.92 g). It had $\bar{M}_n$ = 200 000, and elemental analysis indicated that it contained 5.19 mmol of bromo groups/g (DF = 0.92). Anal. Found: Br, 41.4, 41.7.

Brominated linear polystyrene was reacted with Li and diphenylphosphinous chloride as described by Relles and Schluenz.[14] In a typical experiment brominated polystyrene (24.0 g, DF = 0.92) gave phosphine polymer (31.5 g) which by elemental analysis contained 2.69 mmol of residues 1/g (DF = 0.57) and 0.16 mmol of bromo groups/g (DF = 0.03). It had $\bar{M}_n$ = 90 000. Anal. Found: P. 8.34; Br, 1.25.

Small-Scale Reactions Involving the Conversion of Octan-1-ol into 1-Chlorooctane. The reactions summarized in Tables I, V, and VII were carried out under nitrogen with vigorous stirring by using the quantities of reactants and the reaction conditions indicated in the tables. At the end of the reaction periods the polymers were filtered off and washed several times with the reaction solvent. The filtrate and washings were combined, and a known weight of β-methylnaphthalene was added as an internal standard for GLC. The amounts of octan-1-ol, 1-chlorooctane, and, where appropriate, $CHCl_3$ or C_2Cl_4 in the

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[26] Appel, R.; Willms, L. *Chem. Ber.* **1977**, *110*, 3209.

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[28] Michel, W. Dissertation, University of Bonn, 1974; quoted in ref 2, p 802. See also ref 1, p 391.

[29] See, for example: Yaroslavsky, C.; Patchornik, A.; Katchalski, E. *Tetrahedron Lett.* **1970**, 3629.

[30] "Vogel's Textbook of Quantitative Inorganic Analysis", 4th ed.; Longman: London, 1978; p 342.

mixtures were determined by GLC analyses (with PEGA as the stationary phase at 50 °C for $CHCl_3$ analyses and at 150 °C for the other components).

Reactions Summarized in Table II. The yields from several of these reactions were estimated by GLC analysis by using a procedure similar to that outlined above. In other cases the products were isolated and shown to have melting or boiling points or and spectroscopic data in agreement with literature data. The following examples are typical.

(a) Preparation of 1-Chlorooctane. A mixture of octan-1-ol (651 mg, 5.0 mmol), 1% cross-linked polymer (4.00 g, 2.50 mmol of phosphine/g), and CCl_4 (60 mL) was heated under reflux under nitrogen for 1.5 h. The cooled reaction mixture was filtered and the resin washed several times with CCl_4. The filtrate and washings were combined and most of the CCl_4 distilled off at atmospheric pressure through a fractionating column. Short-path distillation of the residue gave 1-chlorooctane: 565 mg (76%); bp 179–183 °C (755 mm) [lit.[31] bp 181.5 °C (765mm)]. It had IR and ^{1}H NMR spectra identical with those of an authentic sample.

(b) Preparation of 24-Chloro-5β-cholane. 5β-Cholan-24-ol was obtained by converting dehydrocholic acid into 5β-cholanic acid[32] and reducing the latter with lithium aluminium hydride.[33] A mixture of 5β-cholan-24-ol (182 mg, 0.74 mmol), 1% cross-linked polymer 1 (600 mg, 2.50 mmol of phosphine/g), and CCl_4 (10 mL) was vigorously stirred and heated under reflux for 2.5 h. The mixture was cooled and filtered, and the resin was washed several times with CCl_4. Evaporation of the combined filtrate and washings to dryness gave a crystalline product (192 mg). Recrystallization from aqueous acetone gave 24-chloro-5β-cholane: 153 mg (78%); mp 74–75 °C (lit.[33] mp 74–76 °C). The crude product had IR and ^{1}H NMR spectra identical with those of the recrystallized material.

(c) Preparation of 1-Chlorooctadecane. A solution of octadecan-1-ol (1.35 g, 5.0 mmol) and linear polymer 1 (3.71 g, 2.69 mmol of phosphine/g) in CCl_4 (60 mL) was heated under reflux for 2 h. After approximately 30 min the polymer began to precipitate, and at the end of the reaction period it was removed by filtration. Evaporation of the solvent from the filtrate gave a clear oil (1.48 g). Short-path distillation gave 1-chlorooctadecane: 1.10 g (76%); bp 190–195 °C (20 mm) [lit.[31] bp 185–190 °C (15 mm)]; IR and ^{1}H NMR spectra identical with those of an authentic sample.

Reactions Summarized in Tables III and IV. These reactions were carried out under nitrogen by using the quantities of reactants and the reaction conditions indicated in the tables. In all cases the amides or esters were isolated and had melting points in agreement with literature values. The following procedures are typical.

(a) Preparation of β-Naphthoyl Chloride. A mixture of β-naphthoic acid (172 mg, 1.00 mmol), 1% cross-linked phosphine resin 1 (800 mg, 2.00 mmol of phosphine), and CCl_4 (20 mL) was heated under reflux for 4 h. The resin was filtered off and washed several times with CCl_4. The filtrate and washings were combined, and an IR spectrum of the mixture measured. This showed the presence of acid chloride (band at 1762 cm^{-1}) and a trace of acid (band at 1695 cm^{-1}). Methanol (5 mL) was added to the reaction product, and it was heated under reflux for 1 h. The reaction mixture was worked up to give neutral and acid fractions. The neutral fraction consisted of methyl β-naphthoate: 156 mg (84%); mp 75–77 °C (lit.[31] mp 77 °C). The acid fraction was recovered starting material (19 mg, 11%), identified by melting point and IR spectrum.

(b) Preparation of Phenoxyacetanilide. A mixture of phenoxyacetic acid (152 mg, 1.00 mmol), 1% cross-linked phosphine resin (800 mg, 2.00 mmol of phosphine), aniline (205 mg, 2.20 mmol, freshly distilled), and CCl_4 in $ClCH_2CH_2Cl$ (20 mL, 10% v/v) was heated under reflux for 3 h. The cooled mixture was filtered and the solid material washed several times with CCl_4. The filtrate and washings were combined, and solvent was evaporated. The residue was dissolved in ether (25 mL), and the solution was successively washed with saturated aqueous $KHCO_3$, 2 N HCl, and water and then dried ($MgSO_4$). Evaporation of the ether gave phenoxyacetanilide: 163 mg (72%); mp 98–100 °C (lit.[31] mp 101.5 °C).

Preparation of Diphenyl(4-isopropylphenyl)phosphine (4). Isopropylbenzene (1.2 mol) was treated with Br_2 (1.0 mol) in $CHCl_3$ (200 mL) at 0 °C for 2 h. Distillation of the reaction mixture gave 4-bromoisopropylbenzene: 110 g (55% based on bromine); bp 214–218 °C (756 mm) (lit.[31] bp 216 °C). A portion (49.7 g) was treated with Mg and then diphenylphosphinous chloride, following the method described for the preparation of (4-bromophenyl)diphenylphosphine.[34] The product [35.5 g (47%); bp 196–200 °C (2mm)] was induced to crystallize by allowing it to stand in MeOH at −10 °C for 20 h. Recrystallization from EtOH by using seed crystals gave 4: mp 48–49 °C; ^{1}H NMR ($CDCl_3$) δ 1.23 (d, J = 9 Hz, 6 H), 2.90 (quintet, J = 9 Hz, 1 H), 7.20–7.40 (m, 14 H). Anal. Calcd for $C_{21}H_{21}P$: C, 82.87; H, 6.95; P, 10.18. Found: C, 82.99; H, 6.85; P, 10.38.

Preparation of 4,4,4-Triphenylbutan-1-ol. 4,4,4-Triphenylbut-1-ene was prepared from trityl chloride and allyl chloride by the method of Nesmeyanov and Perevalova.[35] The olefin was hydroborated and the product treated with alkaline H_2O_2 by the method of Starnes,[36] except that instead of generating the borane in situ a preformed solution in THF was used. The 4,4,4-triphenylbutan-1-ol had a melting point of 120–122 °C (lit.[36] mp 122–123 °C). The IR and ^{1}H NMR spectra were in excellent agreement with those reported by Starnes.[36]

Substrate Competition. 4,4,4-Triphenylbutan-1-ol (302 mg, 1.0 mmol) and octan-1-ol (130 mg, 1.0 mmol) in CCl_4 (5 mL) were stirred under reflux with 1% cross-linked polymer (800 mg, 2.0 mmol of phosphine) for 2 h. The mixture was cooled, and the resin was filtered off and washed twice with CCl_4. The combined filtrate and washings were analyzed for octan-1-ol and 1-chlorooctane by using GLC as above and for 4,4,4-triphenylbutan-1-ol and the corresponding chloride by using HPLC. A similar experiment using diphenyl(4-isopropylphenyl)phosphine (4; 588 mg, 2.0 mmol) instead of the resin was also carried out. The results are as given in the Results and Discussion.

Recovery of Spent Linear Polymer 1. A solution of octan-1-ol (1.04 g, 8 mmol) and linear phosphine polymer (1.15 g, 3.45 mmol) in CCl_4 (20 mL) was vigorously stirred and heated under reflux for 2 h. The mixture was cooled and added to hexane (250 mL), and the precipitate was filtered off. The polymer was dissolved in CH_2Cl_2 (25 mL) and reprecipitated into hexane (250 mL). The product (1.22 g) was collected and dried. By elemental analysis it contained 0.83 chlorine atoms/phosphorus atom. Anal. Found: P, 6.3, 6.8; Cl, 6.3, 6.2.

Approximately 10-mg samples of the polymer were added to 2-mL portions of various solvents. The polymer dissolved in CH_2Cl_2, $CHCl_3$, and MeOH. It did not dissolve in Me_2CO or $PhCH_3$.

A sample of linear phosphine polymer (3.00 mmol of P/g) was oxidized to the corresponding phosphine oxide polymer as describved by Relles and Schleunz.[14] By use of a test similar to the above, the product was soluble in CH_2Cl_2 and $CHCl_3$ but insoluble in MeOH, Me_2CO, or $PhCH_3$.

Attempted Regeneration of Spent 1% Cross-Linked Phosphine Polymer. Cross-linked phosphine polymer (1%; 3.024 g, 6.80 mmol) was used to convert octan-1-ol into 1-chlorooctane by following the usual procedure. The spent polymer was washed with CCl_4 and then dried. A mixture of the dry polymer, Cl_3SiH (10 g) and Et_3N (10 g) in dry benzene (50 mL) was vigorously stirred and heated under reflux under nitrogen for 24 h. The polymer was filtered off, washed successively with benzene, THF, 30% aqueous NaOH, water, THF, and CH_2Cl_2, and then dried. The "regenerated" polymer was then used to convert octan-1-ol to 1-chlorooctane in the usual manner. One gram of the original polymer could convert 1.12 mmol of octan-1-ol into 1-chlorooctane, but 1 g of the "regenerated" polymer could convert only 0.41 mmol of octan-1-ol into 1-chlorooctane.

Reaction between Benzaldehyde, 1% Cross-Linked Phosphine Polymer, and Carbon Tetrachloride. Benz-

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aldehyde (106 mg, 1.00 mmol), 1% cross-linked phosphine polymer 1 (400 mg, 1.00 mmol), and CCl_4 (5 mL) were stirred under reflux under nitrogen for 4 h. The polymer was filtered off and washed in the usual way. GLC analysis of the products (with an SE-30 stationary phase at 180 °C) indicated the presence of benzal chloride (50 mg, 62% of the theoretical maximum), β,β-dichlorostyrene (52 mg, 60% of the theoretical maximum), and benzaldehyde (11 mg, 10% recovered).

Reactions Summarized in Table VI and Figures 1 and 2. A mixture of the substrate (1.00 mmol) and phosphine (2.00 mmol) in CCl_4 (10 or 30 mL as indicated in the table) was vigorously stirred in a stoppered reaction tube (1 in. wide × 4 in. deep) immersed above the level of the solvent in a thermostated (±0.5 °C) oil bath. For reactions monitored by GLC the 1% cross-linked polymer used contained 2.50 mmol of phosphine/g, and the linear polymer used contained 2.42 mmol of phosphine/g. For reactions monitored by HPLC the 1% cross-linked polymer used contained 2.42 mmol of phosphine/g, and the linear polymer used contained 2.69 mmol of phosphine/g. For reactions monitored by IR spectroscopy the 1% cross-linked polymer contained 2.50 mmol of phosphine/g. Periodically (see Figures 1 and 2 as examples) small samples (<0.05 mL) were removed from the reaction mixtures and analyzed by GLC, HPLC, or IR spectroscopy as indicated in Table VI. When reactions were monitored by GLC, a small known amount of β-methylnaphthalene was added to the reaction mixture to serve as an internal standard. IR analyses were carried out by comparing the areas of the carbonyl peaks in the 1650–1900-cm^{-1} region due to carboxylic acid and acyl chloride. Each reaction was carried out at least twice. The yields of alkyl chloride from a given reaction were found to be reproducible to ±5% of the values given. The yields of acyl chloride from a given reaction were reproducible to ±20% of the values given.

Acknowledgment. We thank the SERC for financial support.

Registry No. Octan-1-ol, 111-87-5; hexadecan-1-ol, 36653-82-4; octadecan-1-ol, 112-92-5; 3-phenylpropan-1-ol, 122-97-4; 4,4,4-triphenylbutan-1-ol, 16778-07-7; 5β-cholan-24-ol, 3110-99-4; 2-*n*-butoxyethanol, 111-76-2; 4-(hydroxymethyl)-2,2-dimethyldioxolane, 100-79-8; cinnamyl alcohol, 104-54-1; benzyl alcohol, 100-51-6; *p*-chlorobenzyl alcohol, 873-76-7; octan-2-ol, 123-96-6; cyclohexanol, 108-93-0; octadecanethiol, 2885-00-9; 3-phenylpropanethiol, 24734-68-7; phenylmethanethiol, 100-53-8; *n*-octanoic acid, 124-07-2; phenylacetic acid, 103-82-2; stearic acid, 57-11-4; phenoxyacetic acid, 122-59-8; 3-*O*-acetyllithocholic acid, 4057-84-5; cinnamic acid, 621-82-9; benzoic acid, 65-85-0; β-naphthoic acid, 93-09-4; α-furoic acid, 88-14-2; aniline, 62-53-3; *p*-toluidine, 106-49-0.

Decomposition Rates, Synthesis, and Spectral Properties of a Series of Alkyl Hyponitrites

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A number of *trans*-alkyl hyponitrites (RON=NOR) were synthesized and characterized. At 66.1 ± 0.1 °C in isooctane and with millimolar to micromolar concentrations first-order kinetics were observed with half-lives (min) of 12.8 ± 0.2 (CH_3), 32.3 ± 1.1 (2-C_3H_7), 15.0 ± 0.3 (cyclohexyl), 25.2 ± 1.2 (*tert*-butyl), 18.3 ± 0.3 (*tert*-pentyl), 3.0 ± 0.1 (benzyl), 11.2 ± 0.5 (2-phenylethyl), and 5.5 ± 0.3 (1-phenylethyl). The rate constants were concentration independent and showed little change with changes in solvent polarity or viscosity. Ultraviolet, magnetic resonance, infrared, and mass spectra for the new hyponitrites are reported. Most of the hyponitrites were highly crystalline solids that could be stored for long periods without change below 0 °C.

Introduction

Organic hyponitrites are convenient, low-temperature thermal and photochemical sources of alkoxyl radicals.[1] With the exception of benzyl hyponitrite,[3] there are virtually no quantitative studies of the rates of decomposition of the nontertiary alkyl esters in the literature,[4] and only sporadic information concerning their spectral properties. Recently an X-ray structure determination and an analysis of the vibrational spectra of *tert*-butyl hyponitrite were reported.[2b] In the present work we present the synthesis, decomposition rates and products, and additional spectral data on the lower alkyl hyponitrites.

Experimental Section

For chemiluminescence studies, water from a constant-temperature bath (Poly Temp Model 80) circulated through the jacket of a Pyrex cell containing the sample in 4–6 mL of solvent. The reaction cell contained a cap provided with inlet and exit tubes to permit flushing the sample with nitrogen and with a well extending to the bottom of the cell for a thermocouple wire. The cell was contained in a blackened box 6 in. on a side. One side of the box had an opening through which light was detected with a Hamamatsu Model R562 PMT, operated at 950 V in a PRF Model TE104TSRF constant-temperature housing. The housing as purchased contained a built-in amplifier–dicriminator. Data were recorded at appropriate intervals (40–150 s) in the photon-counting mode with a HP5316A frequency counter and an Omega Model 410A digital thermometer, both of which were integrated with an Apple II computer for data storage in text files and subsequent analysis.

Kinetic studies by HPLC were carried out with solutions of hyponitrites in 10- or 25-mL volumetric flasks immersed in the constant temperature bath. Aliquots were periodically withdrawn

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[1] A number of references to the hyponitrite literature were given in two recent papers.[2] This paper was presented at the 186th ACS National Meeting, March 20–25, 1983.

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