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Quaternary ammonium polychlorides as efficient reagents for chlorination of unsaturated compounds

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Chlorination of unsaturated compounds by benzyltributylammonium polychlorides results in higher yields of addition products compared to those obtained with molecular chlorine.

Key words: chlorination, olefins, quaternary ammonium polychlorides.

The adducts of halogens with halides of quaternary ammonium bases (QAB) are of interest for preparative organic synthesis as mild halogenating reagents.¹⁻⁵ The interaction of these adducts with a broad range of unsaturated compounds results predominantly in anti-addition products. An extensive study of the properties of tetrabutylammonium dichlorobromide and tribromide made it possible to conclude that these salts act as individual halogenating reagents rather than sources of a molecular halogen. It has been reported^{6,7} that the efficiency of additive chlorination of lower olefins increases upon introduction of QAB chlorides into the reaction medium; however, information on the chlorinating properties of quaternary ammonium polychlorides can hardly be found in the literature, except for one study⁸ describing the reaction of tetrabutylammonium trichloride with styrene. This is apparently due to the common opinion that polychlorides are relatively unstable compared to bromides. However, our studies^{9,10} showed that QAB trichlorides and pentachlorides are quite stable compounds.

The purpose of the present work was to study reactions of unsaturated compounds with QAB polychlorides and also to elucidate the influence of the nature of the solvent used on the ratio of the reaction products.

Experimental

Benzyltributylammonium (BTBA) chloride was prepared by heating equimolar amounts of freshly distilled Bu₃N ("analytically pure") and PhCH₂Cl ("analytically pure") in benzene in a sealed tube at 90 °C for 20 h. The salt that precipitated after cooling the reaction mixture was recrystallized twice from dry benzene and stored in vacuo. Found (%): C, 73.36; H, 11.10; N, 4.68. C19H34CIN. Calculated (%): C, 73.26; H, 11.01; N, 4.50. Chlorine was obtained by thermal decomposition of dehydrated cupric chloride. The absence of water and HCl was confirmed by the absence of characteristic bands in the IR spectra. 1,2-Dichloroethane (DCE) ("chemically pure") was kept over solid KOH and then distilled over P2O5. CCl4 ("chemically pure") and CH2Cl2 ("chemically pure") were distilled over P2O5. Isobutene from a cylinder was subjected to repeated low-temperature vacuum distillation at -93 °C. Its purity was checked by gas adsorption chromatography. The reagent used in the experiments contained >95% of the major compound. Hex-1-ene ("pure") was distilled over CaH₂ in the atmosphere of dry nitrogen. The reagent used contained >99% of the major substance. Cyclohexene ("chemi-

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cally pure") was freed from peroxides by shaking with an acidified aqueous solution of KI, washed with a solution of Na₂S₂O₃ and distilled water, dried with CaCl₂ and Na, and distilled over Na under dry argon; the reagent used contained \sim 99% of the major compound. Styrene ("analytically pure") was distilled in a flow of dry nitrogen with addition of PEG-400; the reagent used contained \geq 99% of the major compound. Phenylacetylene ("pure") was distilled in a flow of dry nitrogen to dry nitrogen with addition of PEG-400; the reagent used in the experiments contained \geq 95% of the major compound. The purity of the organic compounds was checked by GLC.

The NMR spectra of the reaction products were recorded on Varian VXR-400 (¹H, 400 MHz and ¹³C, 100 MHz) and FT-80A (¹H, 80 MHz) spectrometers. The chemical shifts are presented in the δ scale relative to Me₄Si. The IR spectra of solutions were recorded on a Specord 75-IR instrument. Chromatographic analysis was carried out on Chrom-5 and Model 3700 chromatographs with flame ionization detectors. Columns with Apiezon L (5%, l = 2 m, Celite), TKF (10%, l =1.5 m, Chromosorb), and SE-30 (5%, l = 1.8 m, Chromaton) as stationary phases were used. The temperature of the column was varied from 50 to 200 °C depending on the properties of the phase. The retention indices (Kovats indices) of the reaction products I_l^f on a phase f at temperature t/°C were determined from the known formula.¹¹

Chlorination of unsaturated compounds was carried out at ~20 °C in the following way. BTBA polychlorides of a specified composition with the general formula $Bu_3(PhCH_2)NCl \cdot nCl_2$ (n = 1 corresponds to BTBA trichloride and n = 2, to BTBA pentachloride) were synthesized by a previously described⁹ procedure.[•] Excess Cl_2 was displaced from the tube with the reactant by dry air, and then a solution of an olefin in CCl_4 , CH_2Cl_2 , or DCE was added to the tube. When the reaction had been completed (this was judged by the disappearance of the typical color of BTBA polychloride), the resulting solution was washed to remove the salt, hydrogen chloride, and residual chlorine, dried, and analyzed by GLC and ¹H NMR spectroscopy. The composition of the products formed upon passing a slow flow of isobutene through the bulk of BTBA polychloride without a solvent at ~20 °C was also determined.

Chlorination with molecular chlorine was carried out by mixing a solution of the substrate with a solution of molecular chlorine at -20 °C.

Results and Discussion

The reactions of olefins with BTBA polychlorides occur vigorously; therefore, the substrates were used as solutions in DCE, CH_2Cl_2 , or CCl_4 . In the case of DCE and CH_2Cl_2 , BTBA polychlorides gradually dissolved after mixing of the reactants and short-term shaking of the mixture, and the reaction proceeded in a homogeneous solution; after completion of the reaction, the solution remained homogeneous.

In the case of CCl_4 , the reaction occurred at the interface even after shaking. When the reaction had been completed, two liquid layers could be clearly observed in the reaction vessel: the lower layer contained a

solution of the reaction products and the starting olefin, whereas the upper layer was most likely a saturated solution of CCl_4 in BTBA chloride.

For comparison, in addition to the reaction of unsaturated compounds with BTBA polychlorides, blank experiments on the chlorination of substrates with molecular chlorine under similar conditions were also carried out.

Chlorination of isobutene. It is known¹² that dark chlorination of isobutene (1) in low-polarity media yields mostly methallyl chloride (2) resulting from allylic substitution, irrespective of the presence of radical inhibitors in the system. The yield of the addition product, 1,2-dichloro-2-methylpropane (3), is up to 13%, and traces of a poorly separable mixture of a vinylic substitution product, 1-chloro-2-methylprop-1-ene, and tert-butyl chloride (4a + 4b) were also formed. (The presence of tert-butyl chloride among the reaction products was detected based on the ¹H NMR spectra; however, its quantitative determination proved to be difficult.) The chlorination of isobutene in CCl₄ without any additives also yielded three products, which were identified based on the retention times (in the order of their emergence from a nonpolar phase) as 4a + 4b, 2, and 3 (Scheme 1). The retention indices of these compounds on Apiezon L $(I_{50}^{Ap-L\pm5})$ are 532, 624, and 733, and those on SE-30 $(I_{50}^{SE-30}\pm5)$ are 525, 615, and 730. The reaction occurs almost instantaneously and is accompanied by evolution of a large amount of HCl, as indicated by the formation of the typical "fog." The total yield of 2, 4, and *tert*-butyl chloridc (detected by ¹H NMR spectroscopy), which is formed upon hydrochlorination of isobutene and cannot be distinguished from the former two products under conditions of our analysis, reaches 94%; the proportion of 2 is more than 80% (Table 1).

Scheme 1



The reaction of BTBA polychlorides with a solution of isobutene in CCl_4 is completed over 10-20 min, probably due to the fact that it occurs at the interface. Its mechanism might differ from the mechanism of the

^{*} It should be noted that the compositions of the adducts used in reality did not strictly correspond to the compositions presented here; the *n* values were fractional and closer either to 1 or to 2 (see Ref. 9).

BTBA chloride,	Cl ₂ , N/mmol	Calculated adduct	Isobutene, N/mmol	Concentration of the olefin solution	Product ratio (%)				
N/mmol		composition		/mol L ⁻¹	2	3	4a and 4b	5	
0.0	1.24		2.67	1.33	77	6	17		
0.99	1.16	R ₄ NCl ₃	2.67	1.33	9	69	3	19	
0.16	0.66	R4NCIS	0.21	5.35	8	74	Traces	18	
0.19	0.69	R4NCI5	~2 ^b		3	34	1	62	

Table 1. Results of chlorination of isobutene by molecular chlorine and by the adducts^a of chlorine with BTBA chloride in CCl₄

^a Here and in Tables 2-5, the initial salt-to-chlorine ratios in the synthesis of BTBA polychlorides are given; the compositions of polychlorides are given with allowance for the conditions of their synthesis.⁹

^b Gaseous olefin was passed through a mixture of an adduct of chlorine with BTBA chloride. The solvent was added after completion of contact of isobutene with BTBA polychloride.

reaction with molecular chlorine in a homogeneous solution, which is indicated by a substantially different product distribution and the formation of compound 5. The latter was identified based on the retention index as 1,2,3-trichloro-2-methylpropane ($I_{65}^{\text{SE-30}} = 930\pm20$; the index calculated using the additive scheme was 960 ± 30).

It can be seen from Table 1 that the use of BTBA polychlorides results in a considerably higher yield of the addition product 3. The product ratios obtained using adducts with different compositions, $R_4NC1 \cdot Cl_2$ and $R_4NC1 \cdot 2Cl_2$, do not differ substantially. The formation of large amounts of 5 points to a high rate of addition of chlorine to the double bond in molecule 2 in the presence of BTBA polychlorides.

It can be seen that the major product of the reaction of isobutene with BTBA polychloride without a solvent is the trichloride. This might be due to the fact that the molecular chlorine present in the system reacts with the alkene to give compounds 2 and 4. Chlorination of 2 with BTBA polychlorides affords 5. When the alkene is used as a solution, the latter reaction proceeds apparently more smoothly.

Chlorination of styrene. The reaction of styrene (6) with molecular chlorine (Scheme 2) in low-polarity media gives two products, 1,2-dichloro-1-phenylethane (7) and 1-chloro-2-phenylethylene^{1,13} (8). The product ratio virtually does not depend on the properties of the medium or the temperature. At +10 °C in dichloro-

methane¹ and at -90 °C in $C_2F_4Br_2$,¹³ the proportion of 7 in the product mixture is ~70%. When oxygen is removed from the solution and a radical inhibitor (α -naphthol) is added, the ratio of the yields of 7 and 8 does not change.

Scheme 2

PhCH=CH₂
$$\xrightarrow{Bu_3(PhCH_2)NCI \cdot nCl_2}$$
 PhCHCICH₂CI +
6 7
+ PhCH=CHCI (+ PhCHCICHCI₂)
8 9

The composition of the products obtained in the chlorination of styrene without any compounds added, which we carried out for comparison, was consistent with that reported in the literature: the reaction gives compounds 7 and 8, whose retention indices on Apiezon L $(I_{150}^{Ap-L}\pm 20)$ are 1204 and 1303, while those on SE-30 $(I_{200}^{SE-30}\pm 20)$ are 1110 and 1250 (Table 2). The reaction is accompanied by substantial heat evolution and is completed several seconds after the reactants have been mixed.

Chlorination of styrene with BTBA polychlorides in CCl_4 is completed over a period of several minutes. The yield of the addition product 7 increases from 74% to 85-90% when the adduct $Bu_3(PhCH_2)NCl \cdot Cl_2$ is used

BTBA chloride,	Cl ₂ , N/mmol	Calculated adduct	Styrene, N/mmot	Concentration of the olefin solution/mol L^{-1}	Product ratio (%)			
N/mmoł		composition		(solvent)	7	8	9	
0.0	0.95		1.73	0.35 (CCl ₄)	74	26		
0.0	0.98		2.13	1.06 (DCE)	71	29		
1.68	0.91	R ₄ NCl ₃	1,73	0.35 (CCl ₄)	90	8	2	
1.64	4.06	R ₄ NCl ₃	3.47	0.35 (CCl ₄)	88	10	2	
0.98	0.94	R ₄ NCl ₃	2.13	$1.10 (CCI_4)$	85	9	6	
0.16	0.65	R₄NCl ₅	1.6	1.60 (CCl ₄)	81	2	17	
1.84	3.51	R ₄ NCI ₃	3.47	$1.39 (CH_2Cl_2)$	78	22	Traces	
1.00	0.94	R ₄ NCl ₃	2.13	1.06 (DCE)	75	21	4	

Table 2. Results of chlorination of styrene by molecular chlorine and by the adducts^a of chlorine with BTBA chloride

" See footnote" to Table 1.

or to 81% with Bu₃(PhCH₂)NCl·2Cl₂. The relative decrease in the yield of 7 in the latter experiment is apparently due to partial dissociation of the BTBA pentachloride (which is less stable than the corresponding trichloride) giving free chlorine.

The formation of an additional product, compound 9, as in the case of isobutene, is probably due to the additive chlorination of the substitution product 8. The experimental retention indices for 9 are $I_{150}^{\text{Ap-L}} = 1448\pm20$ and $I_{200}^{\text{SE-30}} = 1350\pm20$. The retention index of 1,1,2-trichloro-2-phenylethane on SE-30 (200 °C) estimated by the increment method¹¹ is equal to 1400±50.

It can be seen from Table 2 that the ratio of the products of chlorination of styrene with BTBA polychlorides depends on the solvent polarity. In dichloromethane ($\varepsilon = 8.93$) and 1,2-dichloroethane ($\varepsilon = 10.27$), the polychlorides are readily soluble, and the reaction occurs in the solution rather than at the interface, as in the case of CCl₄ ($\varepsilon = 2.227$). The resulting product ratio is the same as that observed in the chlorination of styrene without BTBA chlorides.

It is known that chlorination of styrene with tetrabutylammonium trichloride affords only 7 and 8 in 66% and 34% yields, respectively.⁶ The fact that the ratio of the product yields obtained in the study cited is close to the results of chlorination of the alkene with molecular chlorine may be due to dissociation of the polychloride anions in solvents with relatively high dielectric constants; hence, the selectivity of the reaction in this case is determined by the rate of dissociation of the polychloride anions.

Chlorination of phenylacetylene. Phenylacetylene (10) is a convenient substrate for investigation of stereochemistry, because the ratio of products resulting from its chlorination (Scheme 3) depends on the reaction conditions. The reaction of 10 with molecular chlorine in CH_2Cl_2 , gives approximately equal amounts of

Scheme 3

PhC=CH
$$\frac{Bu_{3}(PhCH_{2})NCI \cdot nCI_{2}}{10}$$
 PhC=CCI +
10 11
+
$$\frac{Ph}{CI} = C + \frac{CI}{H} + \frac{Ph}{CI} = C + \frac{H}{CI} + PhCCI_{2}CHCI_{2}$$
14

trans- and cis-addition products (12 and 13) and a substitution product, PhC=CCI (11).¹⁴

Direct photochlorination of 10 in CCl₄ and AcOH occurs with low stereoselectivity and involves extensive chlorination of the alkyne, whereas radical chlorination by PhICl₂ is fairly selective and gives mainly the addition products, among which the proportion of the *trans*-isomer 12 is¹⁵ ~85 %.

The direct dark chlorination of phenylacetylene in CCl₄ in the presence of oxygen yielded compounds whose retention indices on TKF (I_{120} ^{TKF}±30) are 1307, 1467, and 1577; those on Apiczon L (I_{150} ^{Ap-L}±20) are 1134, 1249, and 1323; and those on SE-30 (I_{120} ^{SE-30}±20) are 1084, 1205, and 1260. The reaction products were identified based on their retention indices as substitution product 11 and two addition products, *trans*-1,2-dichloro-1-phenylethylene and *cis*-1,2-dichloro-1-phenylethylene (12 and 13), which is consistent with published results.¹⁵

The reaction of compound 10 with BTBA trichloride gives compounds 11-13 in a different ratio (Table 3), and, in addition, product 14 with the retention index $I_{120}^{\text{TKF}} = 1580 \pm 30$ appears. The ¹H NMR spectrum of the product mixture exhibits five distinct groups of signals. The intense peak with δ 3.05 belongs to the alkyne proton in phenylacetylene.¹⁶ The intense multiplet at δ 7.38 corresponds to the benzene ring protons in the initial alkyne and in the chlorination products. The peaks at δ 6.47 and δ 6.63 were assigned, in conformity with the published data, to protons in trans- and cis-1,2-dichlorophenylethylene 12 and 13, respectively.^{15,17} The ratio of the intensities of these signals is 7 : 1, which is close to the results obtained by chromatography. The proton signal at δ 5.08 is evidently due to an additional product containing an aliphatic hydrogen atom in the vicinity of chlorine. The only possible product that would be heavier than dichlorophenylethylene, according to GLC, is 1,1,2,2-tetrachloro-1-phenylethane. It can be expected that saturation of the carbon-carbon bond would lead to an appreciable displacement of the signal for the aliphatic proton. The ratio of intensities of the signals at δ 6.47 and δ 5.08 is equal to \sim 5 : 1, which is close to the ratio of the yields of products 12 and 14.

Thus, chlorination of phenylacetylene with BTBA trichloride results in the predominance of the *trans*isomer among the addition products and in the formation of compound 14.

Table 3. Results of chlorination of a 1 M solution of phenylacetylene in CCl₄ by molecular chlorine and by the adduct⁴ of chlorine with BTBA chloride

BTBA chloride,	Chlorine, N/mmol	Calculated adduct	Phenylacetylenc, N/mmol	Product ratio (%)			
N/mmol		composition		11	12	13	14
	1.01		2.00	18	46	36	
2.50	2.30	R ₄ NCl ₃	4.92	17	59	11	13

" See footnote" to Table 1.

BTBA chloride,	Chlorine, N/mmol	Calculated adduct	Hex-1-enc, N/mmol	Concentration of an olefin solution /mol L ⁻¹		Pro	oduct ra (%)	tio	
N/mmoł		composition		(solvent)	16	17	18	19	20
	1.36	-	2.09	1.25 (CCi ₄)	Traces	28	18	44	
1.02	1.22	R ₄ NCl ₃	2.00	1.00 (CCl ₄)	Traces	15	17	65	3
1.06	1.29	R ₄ NCl ₃	2.00	1.00 (DCE)	Traces	26	26	46	2

Table 4. Results of chlorination of hex-1-ene by molecular chlorine and by the adducts^a of chlorine and BTBA chloride

^a See footnote^a to Table 1.

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Chlorination of hex-1-ene. According to published data, hex-1-ene (15) reacts with molecular chlorine at a very high rate.¹⁸ In fact, dark chlorination of the alkene in CCl_4 under our conditions was completed over a period of less than a second. 3-Chlorohex-1-ene (16), *trans*- and *cis*-1-chlorohex-2-enes (17 and 18), and 1,2-dichlorohexane (19) were detected among the reaction products (Scheme 4).

Scheme 4

Reaction with cyclohexene. Chlorination of cyclohexene (21) with free chlorine has been studied in detail previously.¹² In low-polarity solvents, the reaction occurs simultaneously by free-radical and ionic mechanisms. The major reaction products are *trans*-1,2-dichlorocyclohexane (22), 3-chlorocyclohexene (23), and 4-chlorocyclohexene (24) (Scheme 5).





In the case where hex-1-ene reacts with BTBA trichloride, the reaction gives one more product 20, which was identified as 1,2,3-trichlorohexane (Table 4). On passing to DCE, no significant redistribution of products 16–19 is observed. The retention indices of 16–20 on SE-30 (I_{70} SE-30±5) were 851, 930, 947, 974, and 1038, respectively.

When CCl₄ is used as the solvent, the reaction proceeds much more slowly than in polar 1,2-dichloroethane (several tens of minutes and several minutes, respectively), and, as in the case of other unsaturated compounds, the proportion of the addition product 19 increases. This finding can be explained by the fact that in CCl₄, the degree of dissociation of the polychloride with liberation of chlorine is lower than that in DCE, *i.e.*, the concentration of free halogen in the system is lower.



When cyclohexene was chlorinated with molecular chlorine in CCl_4 in the presence of oxygen, only two products formed in a ratio close to 5 : 1 were detected; based on the retention times, they were identified as 22 and 23 (Table 5).

When cyclohexene was made to react with $Bu_3PhCH_2NCI \cdot Cl_2$, the proportion of the allylic substitution product 23 sharply decreased. The ¹H NMR spectrum of the reaction mixture displays four intense multiplets corresponding to dichloride 22. The low-field

Table 5. Results of chlorination of a 0.00487 M solution of cyclohexene in CCl₄ by molecular chlorine and by the adduct^a of chlorine with BTBA chloride

BTBA	Chlorine,	Calculated adduct	Concentration	Produc	ct ratio
chloride	, N		of an olefin	(9	8)
/nmol	/mmoi	tion	/mol L ⁻¹	22	23
0.0	7.91	R ₄ NCl ₃	0.487	83	17
2.43	7.91		0.487	96	4

" See footnote" to Table 1.

spectral region contains signals for the two protons of the CHCl groups at δ 4.01 (cf. Ref. 19). The multiplet for the proton of the CHCl group in chloride 23 manifests itself at δ 4.62 and has a relative integral intensity of 0.03. The same intensity was found for the multiplets at δ 5.80 and δ 5.87 corresponding to the olefinic protons.

Chlorination of norbornene. Norbornene (25) is¹⁴ a classical model substrate used to study the mechanism of addition to C=C double bonds. Chlorination of 25 (Scheme 6) was studied in most detail by Poutsma,²⁰ who elucidated the regularities of the variation of the product ratios for radical and ionic chlorination mechanisms.





In the presence of BTBA trichloride, the composition of the reaction mixture substantially changes. The yield of products 26 and 27 formed in a ratio of $\sim 1 : 1$ amounts to 94% of the total yield. The analysis was based on the ¹³C NMR spectrum of the reaction mixture, which was compared with the spectra of known chlorinated derivatives of norbornane.²¹ Products 28— 31 were totally missing, indicating that in the presence of BTBA polychlorides, the reaction is more selective. This product distribution allows the chlorinating reagent under study to be classified as an "efficiently strong" electrophile.

To summarize the results obtained here, it should be noted that the use of individual BTBA polychlorides in reactions with unsaturated compounds able to undergo both additive and substitutive chlorination results in substantially increased yields of additive chlorination products. Moreover, when BTBA polychlorides are used, chlorine adds to the substitution products formed during the reaction at a rate comparable to the rate of chlorination of the initial substrate, even though it is fairly reactive. For the reactions of BTBA polychlorides with phenylacetylene and cyclohexene, it was shown that *trans*-addition is the predominant reaction pathway.

The regularities found provide information for selection of conditions that would enable efficient use of QAB polychlorides in the preparative chlorination of unsaturated compounds, including halogen-containing alkenes.

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