Synthesis of Cationic Surfactants with Alkenyl Group

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ABSTRACT

Quaternary ammonium chlorides with long chain alkenyl groups were synthesized by the reaction of tert-amines with alkylallyl chloride which, in turn, were obtained by the allylic chlorination of 1-olefins with N-tert-butyl- or N-cyclohexyl-N-chloro-ethanesulfonamides. Of the two kinds of alkylallyl chlorides prepared by the allylic chlorination of 1-olefins, the γ-alkylallyl chlorides(I), were found to be reactive with tert-amines, while the secondary chlorides, α-alkylallyl chlorides(II), were not so reactive and, when the allylic chloride mixture was reacted with tert-amine under suitable reaction conditions, the γ-alkylallyl chloride could be selectively converted to a quaternary ammonium chloride while the α-alkylallyl chloride was recovered unreacted. The quaternary ammonium chlorides thus obtained were identified as γ-alkylallyl ammonium chlorides from their spectra, and they were shown to possess almost the same surface tension lowering ability as their saturated homologs, although larger critical micelle concentration values and greater water solubilities were observed.

INTRODUCTION

N-Alkylation of alkenylamines is a possible means for the synthesis of cationic surfactant with alkenyl group. Although a few synthetic methods for the precursary compounds of alkenylamines have been suggested (1-4), these methods generally involve several reaction steps, and it is difficult to get alkenylamines in high overall yields. Furthermore, the synthetic method of quaternary salts from alkenylamines is not applicable to the preparation of some types of cationics such as N-pyridinium- or N-methylmorpholinium salts.

We have been studying the allylic halogenation of long chain 1-olefins with N-halosulfonamides which have a bulky substituent on nitrogen atom, and for the purpose of allylic chlorination, it was found that N-chloro-N tert-butyl- or N-chloro-N-cyclohexyl-ethanesulfonamides are competable to other chlorinating agents such as tert-butyl hypochlorite (5) or N-chloro-N-cyclohexylbenzenesulfonamide (6).

The reactions of allylic chlorides with amines were reviewed by DeWolfe and Young (7). Many studies have been carried out on allyl chloride and alkylallyl chlorides with short alkyl groups (8-10), but reactions with long chain alkylallyl chlorides have not been investigated in detail.

In this investigation we attempted to obtain cationic surface active agents containing an alkenyl group from the reaction between a tertiary amine and an alkylallyl chloride which was actually synthesized as mixtures of α- and γ-allyl isomers. The structure and the surface active properties of the quaternary ammonium chlorides containing alkenyl groups were investigated.

EXPERIMENTAL PROCEDURES

Alkylallyl Chlorides Mixtures

According to the procedures reported in the previous paper (11), a 1-olefin was reacted with N-alkyl-N-chloroethanesulfonamide at 130 C in the presence of benzoyl peroxide. The alkylallyl chlorides were separated by frac-

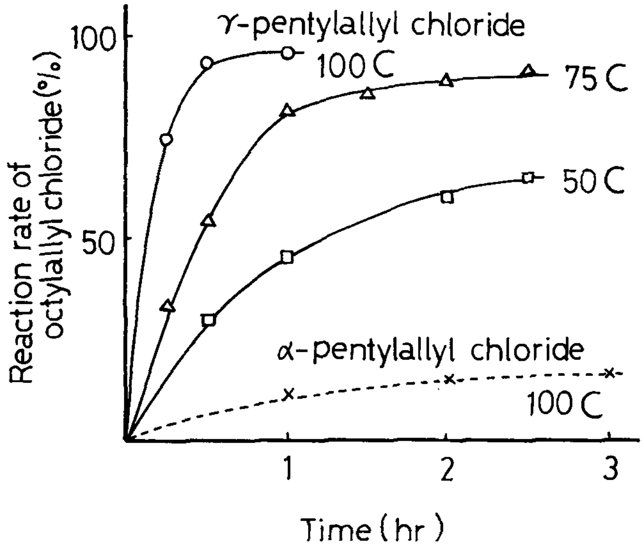


FIG. 1. Effect of temperature on the reaction of octylallyl chloride with pyridine.

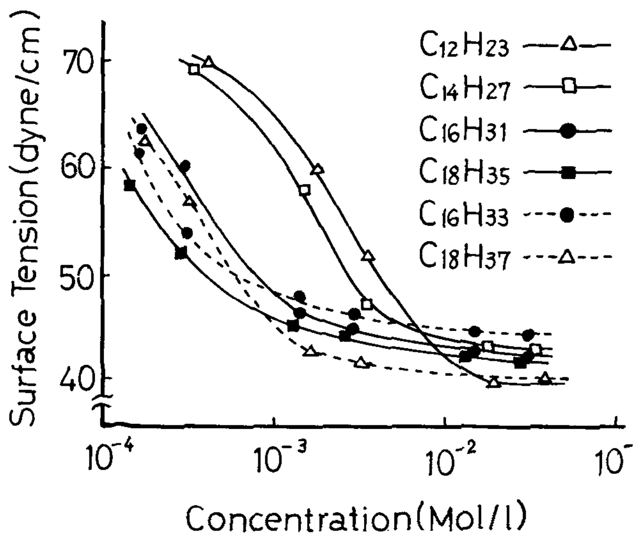


FIG. 2. Surface tension of aqueous solution of γ-alkylallyl pyridinium chloride (25 C).

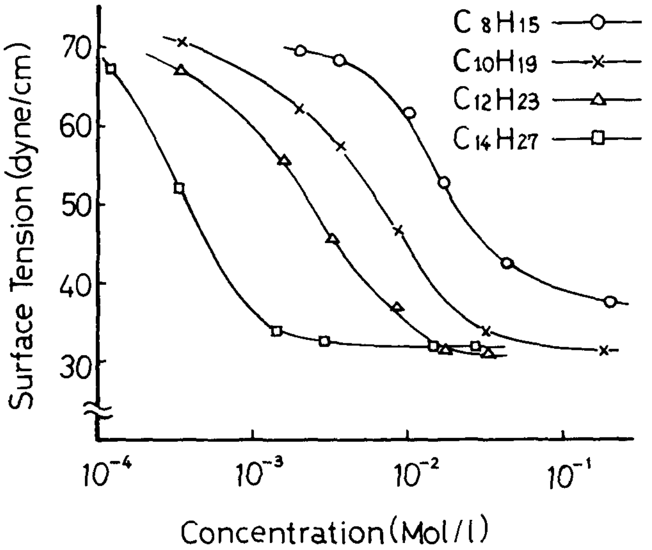


FIG. 3. Surface tension of aqueous solution of γ-alkylallyl N-methylmorpholinium chloride (25 C).

tional distillation at reduced pressure. The analysis of their isomer ratios was conducted by gas liquid chromatography (GLC) with an ionic flame detector using Apiezon Grease L or Silicon Oil as liquid phase. The composition and physical properties of alkylallyl chlorides are summerized in Table I.

Reactivity of Primary and Secondary Allyl Chlorides

A mixture of γ- and α-pentylallyl chlorides (2.0g, 0.014 mol) was mixed with pyridine (2.9 g, 0.032 mol), and the reaction mixture was kept at constant temperature with stirring. The quantities of both components were determined by GLC using 1-dodecene as an internal standard at definite time intervals. The results were shown in Figure 1.

Synthesis of Quaternary Ammonium Chlorides

The alkylallyl chloride mixture (0.01 mol) and pyridine or N-methylmorpholine (0.023~0.027 mol, five times moles for [1]) were mixed and the mixtures were kept at constant temperature for a definite period of time. After the reaction was completed, ether was added to the reaction mixtures, refluxed for 30 min, cooled, and the quaternary ammonium salts were then separated by filtration. Dilute hydrochloric acid was added to the filtrate and the ether layer was separated, washed with water and dried over anhydrous sodium sulfate. The ether was distilled off, and the residue was weighed and analyzed by GLC for the determination of unreacted alkylallyl chlorides.

In the reaction at ordinary temperature, alkenyl chloride mixture was dissolved in ether and allowed to stand until most of the γ-alkylallyl chloride was consumed. The results are summarized in Tables II and III. In these tables, conversion of γ-alkylallyl chloride (I) was calculated on the basis of recovered amount of (I). The crude yields of quaternary ammonium chloride and recovered alkylallyl chlorides were calculated, based on the amounts of alkylallyl chloride mixtures employed in the experiments.

The recovered pentylallyl chloride was distilled at reduced pressure and α-pentylallyl chloride (II) (bp78~80 C/30mm, n^{20}_D 1.4433 [1.44229] [12]) was obtained. γ-Pentylallyl chloride (bp 86 C/37 mm, n^{20}_D 1.44772) was reacted with pyridine in the analogous manner, and pentylallyl pyridinium chloride was obtained in a 90% yield.

The crude quaternary ammonium salts were dissolved in ethanol, decolorized with activated carbon in a dry box and recrystallized from an ethanol-ether or an aceton-ether mixture. They were dried in an Abderhalden apparatus, and the chloride ion content was determined. The pyridinium salts with short alkenyl chain (C_8, C_{10}) were hygroscopic and obtained as semisolids or pastes. The results were shown in Table IV.

Spectral Analyses of Quaternary Ammonium Salts

Spectral data are given for each of the pyridinium- and N-methyl-morpholinium chlorides as examples.

a) *Tetradecenyl pyridinium chloride*: IR (KBr disk, cm^{-1}): 3380, 3070, 2940, 2860, 1670, 1640, 1590, 1490, 1470, 1385, 1210, 1060, 985, 788, 778, 725, 685. NMR (DMSO-d_6, τ): 913 (*t*, 3.0H), 8.75 (*m*, 18.0H), 7.95 (*m*, 1.9H), 4.68 (*m*, 1.9H), 4.10 (*m*, 1.9H), 0.80~1.80 (5H, ring proton).

b) *Octenyl N-methylmorpholinium chloride*: IR (KBr disk, cm^{-1}): 3380, 2940, 2850, 1670, 1475, 1120, 992, 910, 890, 720. NMR (DMSO-d_6,τ): 9.10 (*t*, 3.0H), 8.70 (*m*, 6.2H), 7.85 (*m*,2.2H), 6.55 (*m*+*s*, 6.8H), 6.08 (*m*, 4.0H), 5.74 (*m*, 2.1H), 3.80~4.30 (1.9H).

Measurement of Surface Tension and Water Solubility

a) *Surface tension*: The surface tension of aqueous solution of γ-alkylallyl quaternary ammonium chlorides was measured by Du Nouy's tensiometer at 25 C. Results are shown in Figures 2 and 3. Critical micelle concentration values were obtained from the figures as those concentrations at which the surface tension concentration curves bent (13).

b) *Water solubility*: The temperature at which a 1 wt % aqueous solution became clear was measured. Thus a 0.05 g sample was placed in a test tube equipped with a thermometer and 5.0 ml of water was added. The solution was cooled to 0 C, heated again gradually, and the temperature at which it became clear was determined. The results are shown in Table V.

RESULTS AND DISCUSSION

A mixture of γ- and α-alkylallyl chlorides was obtained by the allylic chlorination of 1-olefins with N-chlorosulfonamides (11).

TABLE I

Composition of Alkylallyl Chlorides

RCl	Boiling point, C/mmHg	Chlorine content,[a] %	Composition, %[b]	
			I	II
$C_8H_{15}Cl$	105~6/65	24.0 (24.2)	57	43
$C_{10}H_{19}Cl$	70.5/6	19.7 (20.3)	50	50
$C_{12}H_{23}Cl$	86~8/5	17.4 (17.5)	44	56
$C_{14}H_{27}Cl$	100~102/0.6	15.3 (15.4)	55	45
$C_{16}H_{31}Cl$	138~140/0.9	12.9 (13.7)	60	40
$C_{18}H_{35}Cl$	165~167/0.9	12.5 (12.4)	---	---

[a] Values in parentheses are calculated values.

[b] Determined by gas liquid chromatography, Silicon DC 550, 10% on Diasolid L. I: γ-Alkylallyl chloride; II: α-alkylallyl chloride. The values for $C_{16}H_{31}Cl$ were calculated on the basis of a NMR spectrum.

TABLE II

Reaction of Alkylallyl Chlorides with Pyridine

Alkylallyl chloride	Composition, %[a]		Reaction conditions[b]		Conversion of I, %	Yield of alkylallyl pyridinium chlorides, %	Recovered alkylallyl chlorides II+I, %
	I	II	Temperature, C	Time, hr			
$C_8H_{15}Cl$	57	43	100	2.5	90	71	32
$C_8H_{15}Cl$	57	43	75	2.5	85	60	37
$C_8H_{15}Cl$	57	43	50	2.5	80	57	45
$C_8H_{15}Cl$	51	49	Room temperature	1600[c]	89	55	44
$C_8H_{15}Cl$	100	0	100	2.5	93	90	5
$C_{10}H_{19}Cl$	50	50	90	3	83	54	49
$C_{12}H_{23}Cl$	44	56	90	4	80	50	52
$C_{14}H_{27}Cl$	55	45	90	4	75	42	59
$C_{16}H_{31}Cl$	—	—	90	4	—	25	—
$C_{18}H_{35}Cl$	—	—	90	4	—	20	—

[a] I: γ-Alkylallyl chloride; II: α-alkylallyl chloride.

[b] Molar ratio, pyridine I: 5.0.

[c] Ether was used as solvent.

TABLE III

Reaction of Alkenyl Chlorides with tert-Amines

Alkylallyl chlorides	Composition,%[a]		tert-Amine	Reaction conditions[b]		Conversion of I, %	Yield of quaternary ammonium chlorides, %	Recovered alkenyl chlorides II+I, %
	I	II		Temperature,C	Time,hr			
$C_8H_{15}Cl$	57	43	N-Methyl Morpholine	90	3	89	49	45
$C_8H_{15}Cl$	57	43	Triethylamine	Room temperature	1650[c]	81	43	52
$C_8H_{15}Cl$	51	49	N-Methyl Morpholine	Room temperature	1600[c]	90	52	48
$C_{10}H_{19}Cl$	50	50	N-Methyl Morpholine	90	3	90	48	47
$C_{12}H_{23}Cl$	44	56	N-Methyl Morpholine	90	4	82	31	72
$C_{14}H_{27}Cl$	55	45	N-Methyl Morpholine	90	4	60	28	70

[a] I: γ-Alkylally chloride; II: α-alkylallyl chloride.

[b] Molar ratio, tert-amine I: 3.7~5.0.

[c] Ether was used as solvent.

TABLE IV

Alkenyl Pyridinium- and Methylmorpholinium Salts

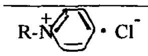
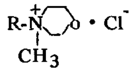
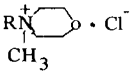
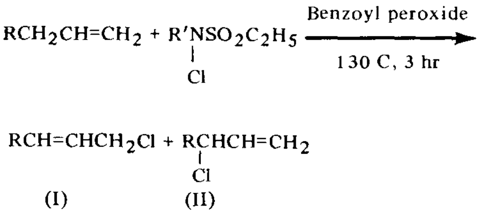
Salts	Appearance	Chlorine content,% Found (calculated)
		
R: $C_{10}H_{19}$	Pale yellow paste	13.1 (13.96)
R: $C_{12}H_{23}$	Pale yellow solid	12.2 (12.57)
R: $C_{14}H_{27}$	White powder	11.1 (11.44)
R: $C_{16}H_{31}$	White powder	9.8 (10.49)
R: $C_{18}H_{35}$	White powder	9.3 (9.68)
		
R: C_8H_{15}	Pale yellow powder	14.4 (14.30)
R: $C_{10}H_{19}$	Pale yellow powder	12.4 (12.85)
R: $C_{12}H_{23}$	Pale yellow powder	11.7 (11.66)
R: $C_{14}H_{27}$	Pale yellow powder	9.9 (10.67)

TABLE V

Critical Micelle Concentration and Solubility of γ-Alkylallyl Quaternary Ammonium Chlorides

Sample	Critical micelle concentration mol/l · 10^3	Krafft point, C
		
R: $C_{18}H_{35}$	0.7	14.5
R: $C_{16}H_{31}$	1.5	<0
R: $C_{14}H_{27}$	4.0	<0
R: $C_{12}H_{23}$	8.5	<0
R: $C_{16}H_{33}$		
		
R: $C_{14}H_{27}$	0.7	<0
R: $C_{12}H_{23}$	6.5	<0
R: $C_{16}H_{33}$	0.6	17.5



$$RCH_2CH{=}CH_2 + \underset{Cl}{R'NSO_2C_2H_5} \xrightarrow[130\text{ C, 3 hr}]{\text{Benzoyl peroxide}} \underset{(I)}{RCH{=}CHCH_2Cl} + \underset{(II)}{\underset{Cl}{RCHCH{=}CH_2}}$$

R': tert-butyl, cyclohexyl

The fraction that contained approximately equal amounts of both isomers (I,II) was obtained by distillation of the crude allylic chloride mixture and used as starting material (Table I).

In order to study the reactivities of the alkylallyl chlorides with a tert-amine, the mixture of γ- and α-alkylallyl chlorides was reacted with excess pyridine. As shown in Figure 1, γ-pentylallyl chloride was found to react rapidly with pyridine at 100 C, while the reaction of α-pentylallyl chloride was observed to be very slow; only ca. 15% of α-pentylallyl chloride was consumed after reaction at 100 C for 3 hr.

From the above results, it was concluded that only the primary chlorides (I) could selectively quaternize tert-amine if suitable reaction conditions were chosen.

For the synthesis of quaternary ammonium salts, the reaction of allylic chlorides with tert-amines was carried out under various reaction conditions as shown in Tables II and III. The temperature was kept below 100 C to avoid the reaction of the secondary chlorides, although in some cases some of the primary chloride (I) remained unreacted at the end of the reaction. In the reaction at relatively higher temperatures (90-100 C), a higher conversion of γ-alkylallyl chloride was attained. However,the reaction mixture was colored markedly, and the secondary chloride was found to be consumed to a considerable extent.

The reaction rate of the allylic chlorides decreased with increasing length of their alkyl chain, and in the reaction of the higher alkylallyl chloride (C_{16} and C_{18}), the yields of quaternary salts were only 20-25% under similar reaction conditions (90 C, 4 hr). However, an analysis of allylic chloride before and after the reaction could not be completed.

The recovered allylic chlorides were found by GLC analysis to consist mainly of α-alkylallyl chlorides (II) which could be purified by distillation under reduced pressure.

The crude quaternary salts were decolorized with activated carbon and purified by recrystallization from aceton-ether or ethanol-ether. Some of the pyridinium salts with short alkylallyl chains were obtained as pastes or semisolids, because they were hygroscopic and difficult to crystallize.

The purity of the salts was determined by analysis of chloride ion content, and their structure was investigated by spectrum analysis (Table IV).

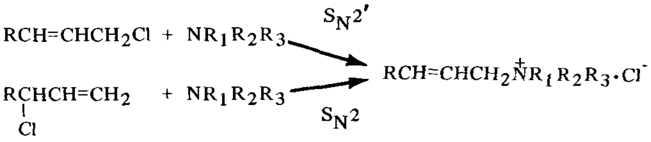
In the NMR spectra of the pyridinium or N-methylmorpholinium chlorides, no absorption that was supposed to be due to the vinyl proton was observed around 910 cm^{-1}.

Furthermore ihe IR spectra of the pyridinium chloride obtained from the mixture of α- and γ-pentylallyl chloride and that of the quaternary pyridinium chloride obtained from γ-pentylallyl chloride were found to be completely identical.

From the above spectral data, the purified quaternary chloride was identified as γ-alkylallyl pyridinium or N-methylmorpholinium chlorides.

The α-alkylallyl chloride (II) was observed to be consumed to some extent in the reaction, the resultant product was possibly a mixture of γ- and α-alkylallyl derivatives.

However, in the reaction of α-methylallyl chloride with *triethylamine* or *trimethylamine* without solvent under relatively mild reaction conditions, it was demonstrated that abnormal displacement (S_N2') occurred preferentially to normal displacement (S_N2) (9,10). In the reaction of alkylallyl chlorides with longer alkyl chains, this tendency is considered to be more remarkable because of steric hindrance.



$$RCH{=}CHCH_2Cl + NR_1R_2R_3 \xrightarrow{S_N2'} RCH{=}CHCH_2\overset{+}{N}R_1R_2R_3{\cdot}Cl^-$$
$$\underset{Cl}{RCHCH{=}CH_2} + NR_1R_2R_3 \xrightarrow[S_N2]{} RCH{=}CHCH_2\overset{+}{N}R_1R_2R_3{\cdot}Cl^-$$

As the stereoisomers of the products were concerned, conclusive results could not be drawn from spectral analyses, although the predominance of *trans* isomer was assumed.

Some surface active properties of these cationics synthesized were determined. The surface tension lowering ability of the aqueous solutions of the pyridinium and N-methylmorpholinium chlorides was, as shown in Figures 2 and 3, found to be almost the same as that of their saturated homologs. However larger critical micelle concentration values were observed, compared with those of corresponding saturated compounds.

The quaternaries that have alkenyl group in the molecule were observed to have good water solubility and their Krafft points were found to be below 0 C, except octadecenyl pyridinium chloride (Table V).

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