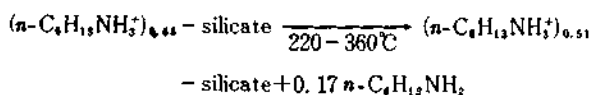


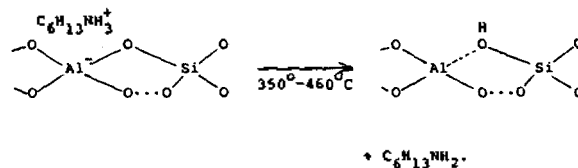
Figure 2. Gas chromatography results of the evolved gas from *n*-hexylammonium -layer silicate(I): (a) at 300°C using carbowax 20M stainless column (5mm × 3m) with TCD; (b) at 400°C using OV-1 (10% doped) stainless column (5mm × 3.6m) with FID.

the retention time with standard *n*-hexylamine. This indicated it was simple deamination, and according to the TG data of this process, approximately 25% of weight decrease of the thermal decomposition except the dehydration step was made. On the basis of this result, the chemical equation of the first step can be simply formulated as follows:



The protons left in the silicate lattice after deamination were considered to combine with the -OH of the octahedral unit to form water because the interlayer oxygens affected by the octahedral replacement were apparently not negative enough to trap protons.⁶

For the second step in which the tetrahedral replacement is participated, the gas chromatography result at 400°C supported that the catalytic alkylchain cleavage was involved in this step, though the fact that the small amount of *n*-hexylamine was evolved suggested the deamination reaction was also simultaneously preceded (Figure 2-b). In this case, the protons are attached to the oxygen atoms bridging Si and Al atoms in tetrahedral sheet where the negative charges are strongly localized to form silanol groups, that is, Brønsted acid sites on the silicate surface.^{6,8}



These active sites and the Lewis acid sites, that is, the tetrahedral replacement centres are considered to catalyze the evolved *n*-hexylamine diffusing out from the interlayer space. The catalytic alkylchain cracking is related with the reaction temperature, which is necessary to obtain the thermal energy for the activation of silicate surface. Because the tetrahedral replacement exhibits stronger ionic bonding character than in the case of the octahedral replacement, the adsorption site originated from the tetrahedral replacement can hold the intercalated *n*-hexylammonium ion on the silicate surface even at the high temperature, which is hardly expected for the site due to octahedral replacement.

In summary, the decomposition reaction pathway of *n*-hexylammonium derivatives can be differentiated by the replacement site determining the nature of the electric field generated on the interlayer surface of layer silicate. The octahedral substitution site induces only deamination at 220–360°C. But the alkylchain cracking catalysis is observed at higher temperature around 350–460°C, which might be strongly affected by the site resulting from tetrahedral replacement.

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Syntheses of Polymer-Bound Hemin, Biliverdin and Bilirubin

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The exact nature of binding between bilirubin and albumin is not known clearly¹, although several types have been suggested: covalent bonding^{2,3}, hydrophobic and electrostatic

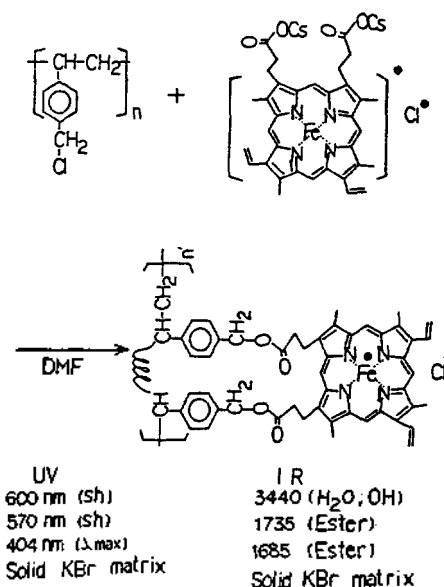
bonding⁴, and salt linkage and hydrogen bonding.^{5,6} In order to study the binding type the polymer bound hemin, biliverdin and bilirubin were synthesized. Only a few papers have ap-

peared involving tetrapyrrole covalently bound to chloromethylated polystyrene.^{7,8} 3-Aminopropylsilated silica gel-bound hemin, biliverdin and bilirubin were prepared by reacting 3-aminopropylsilated silica gel with hemin, biliverdin and bilirubin respectively.⁹

As a preliminary test for the reaction of the polymer with hemin, biliverdin (BV) and bilirubin (BR) a decrease of hemin (or biliverdin, bilirubin) concentration by adding polystyrene in uv cuvette was observed. Hemin was converted to cesium salt by adding cesium bicarbonate. Reaction of this salt with chloromethylated polystyrene (1% cross linked chloromethylated polystyrene, divinylbenzene, Pierce Chemical Co., Rackford, Il., U.S.A.) at 60°C for 20 hrs gave polymer-bound hemin (PCS-Hemin). The carboxylic anion of hemin was attached to the benzyl position of poly(p-chloromethylstyrene) (see Scheme 1). The ir and uv spectral data of solid sample in KBr matrix were given in Table 1. Polymer-bound biliverdin and biliverdin (PSC-BR, PCS-BV) were also prepared by the same method (see Scheme 2, 3 and Table 1).

For the general part of experiment, see the reference 9. The synthetic process is as follows: Hemin (100 mg, 0.15 m mole) was dissolved in 95% ethyl alcohol (7 ml) and 2 ml of H₂O was added. The pH of the solution was adjust to 8.0 with the use of pH-meter by adding cesium bicarbonate. The neutral solution was evaporated by a rotatory evaporator. To the residue was added benzene and repeatedly evaporated to dryness. The dry powder was further dried over P₂O₅ for 10

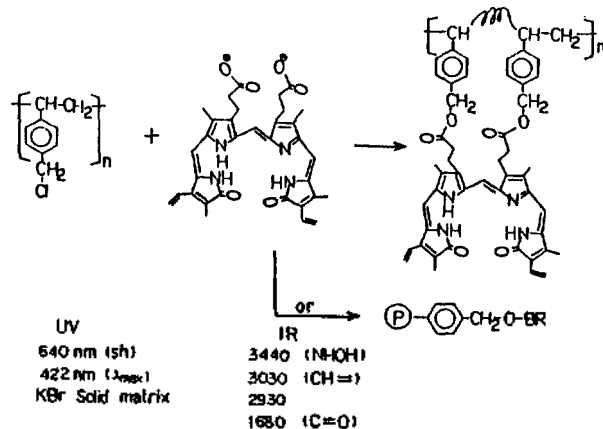
hrs. To the cesium salt was added 4 ml of DMF and 130 mg of chloromethylated polystyrene (0.13 m mol of -CH₂Cl). The mixture was heated to 60°C for 20 hrs while stirring. The resin was filtered and washed thoroughly with DMF, DMF + H₂O and 95% EtOH. The solid was dried over P₂O₅ by vacuum. Product (99 mg) was obtained as black solid.



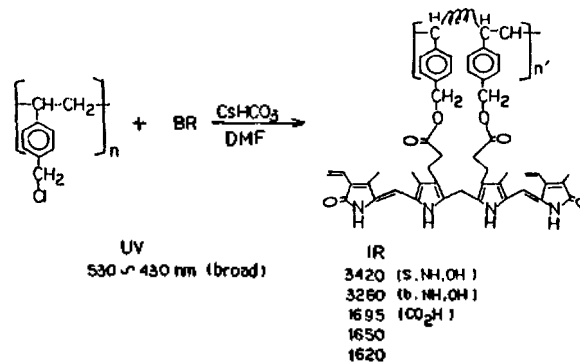
Scheme 1.

Table 1. IR and UV Data of Polymer Bound Hemin, BV and BR

Compds	IR	UV
Hemin	3400 (OH) 1710 (COO)	654 (sh) 550 (λ _{max})
P-Cl Polystyrene (PCS)	940 (OH) 3060 (CH=) 2910 (CH) 1950 1800	454 (sh) <320
PCS-Hemin	3440 (H ₂ O, OH) 1735 (ester) 1685 (ester)	600 (sh) 570 (sh) 404 (λ _{max})
BV	3420 (NH) 1705 (CO ₂) 1600	662 (sh) 378 (λ _{max})
PCS-BV	3440 (NH, OH) 3030 (CH=) 2930 (CH) 1680 (C=O)	640 (sh) 422 (λ _{max})
BR	3420 (OH) 3260 (NH ₂) 1700 (CO ₂) 1650 1615 940	470 (λ _{max})
PCS-BR	3420 (NH, OH) 3260 (b. NH) 1695 (CO ₂ H) 1650 1620	530-430 (b)



Scheme 2.



Scheme 3.

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A Practical Synthesis of (E)- β -Farnesene, the Alarm Pheromone of Aphids

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(E)- β -Farnesene (**1**), (6E)-methylene-7,11-dimethyl-1,6,10-dodecatriene(Figure 1), was known as a constituent of various essential oils.¹ In 1972, W.S. Bowers identified (E)- β -farnesene as an alarm pheromone of cotton aphid, *Aphis gossypii* Glover and other aphid species.² The damage to crops by aphids either by feeding or by transmitting virus disease can be prevented to some extent by insecticides, but aphids are developing increased resistance, particularly to systemic organophosphates.³ The fast-acting pyrethroids may control.⁴ Of the chemicals that influence aphid behavior, the most active is the alarm pheromone,⁵ (E)- β -farnesene(**1**).

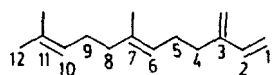
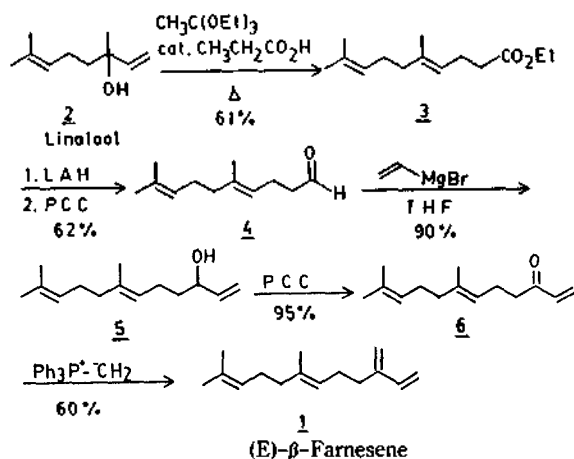
(E)- β -Farnesene

Figure 1.

(E)- β -Farnesene was prepared by dehydration of farnesol and nerolidol with both basic and acidic catalysts.⁶ By dehydration, mixtures including α - and β -farnesene were formed. Several other synthesis have been reported in the literature.⁷



Scheme 1.

Now we wish to report a convenient and practical method to synthesize (E)- β -farnesene using readily available linalool, a monoterpene. The establishment of the (E)-configuration at 6-position of (E)- β -farnesene was accomplished by ortho ester Claisen rearrangement reaction developed by W.S. Johnson.⁸

Ortho ester Claisen reaction of linalool(**2**) with triethylorthoacetate in the presence of a catalytic amount of propionic acid at 140° afforded ethyl (4E)-5,9-dimethyldecanoate(**3**) in 61% yield. The product obtained was distilled on a Kugelrohr under reduced pressure(3mmHg). The ratio of (E)- and (Z)-isomer was 97:3 by HPLC analysis. LAH reduction of the above ester(**3**) followed by PCC oxidation⁹ provided the aldehyde(**4**). The aldehyde was purified by flash chromatography using n-hexane-ethyl acetate(2:1) as eluents. The aldehyde(**4**) was submitted to the addition of vinylmagnesiumbromide in tetrahydrofuran to furnish 7,11-dimethyl-1,6,10-dodecatriene-3-ol(**5**) which was subsequently oxidized with PCC reagent to give α,β -unsaturated ketone(**6**). The α,β -unsaturated ketone(**6**) was purified by flash chromatography using n-hexane-ethyl acetate(1:1) as eluents. This ketone(**6**) was finally subjected to Wittig reaction with methylidene triphenylphosphonium ylide to afford (E)- β -farnesene(**1**) (Scheme 1). The (E)- β -farnesene¹⁰ thus obtained was identical in all respects(TLC,NMR,IR,GC) with the material previously reported in the literature.

This method is considered to be suitable to prepare a fair amount of alarm pheromone to conduct field test experiments.¹¹

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