

Syntheses and Characterizations of Polysilanes with Bulky Substituents

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Several polysilanes with sterically bulky substituents such as poly(2-phenylpropyl)(*n*-hexyl)silane were prepared by Wurtz-type coupling. The polysilane products were mixtures of low-molecular-weight polymers ($M_w \sim 10^3$) as major and high-molecular-weight polymers ($M_w \sim 10^6$) as minor. Overall yields for polysilanes were in the range of 81-99%. λ_{max} of liquid low MW polymers appeared at around 280 nm. Formations of solid high MW polymers were decreased by a longer reaction time and increased steric bulkiness of substituents. High MW polymers with λ_{max} at 327 nm except crosslinked polymers were soluble in common organic solvents and found to be light sensitive. Crosslinked high MW polymer gave 21% TGA ceramic yield, compared with linear high polymer giving zero ceramic yield.

Introduction

Recently, polysilanes have been investigated as a new class of an inorganic polymer for the possible applications such as ceramic precursors, polymeric photoconductors, radiation sensitive materials for high resolution microlithography, and materials with nonlinear optical properties.¹ Polysilanes consist of a linear Si-Si catenation in the main chain and two organic substituents on each silicon atom. One of the most interesting features of the polysilanes is their unusual electronic structure.² All substituted polysilanes absorb strongly in the UV-visible spectral region. σ -Electrons in the main chain of polysilanes are delocalized and is responsible for the electronic properties. Absorption maxima are affected by substituents and chain lengths of polysilanes, due to structural and electronic changes. Most of alkyl- and aryl- substituted derivatives absorb from 290 to 360 nm although some bisarylated materials absorbing out to 400 nm.³

The earliest synthetic procedure for the preparation of substituted polysilanes utilized the Wurtz-type reductive coupling of dichlorosilane derivatives.⁴ Recently, polysilanes have been prepared by dehydrocoupling of monosubstituted silanes using early transition metal catalysts,⁵ ring-opening polymerization of cyclosilanes,⁶ anionic polymerization of masked silanes,⁷ and sonochemical coupling of dichlorosilanes with alkali metals.⁸ Though polysilane synthesis by the reductive coupling of dichlorosilanes with sodium in toluene above 100 °C is known for poor reproducibility, polymodal molecular-weight distributions, and low yield for high-molecular-weight polymer, the Wurtz-type coupling still remains the most effective general procedure for the preparation of high-molecular-weight polysilane derivatives.

Various organic groups were introduced into the polysilanes to give structural and electronic changes. Those were alkyl groups such as *n*-hexyl, *n*-dodecyl, cyclohexyl and aryl groups such as phenyl and tolyl, and electronic properties were measured.^{1,2} However in many cases, those polysilanes were synthesized from corresponding diorganodichlorosilanes which were prepared via difficult synthetic pathways such as Grignard reaction, and therefore the variety of reactant dichlorosilanes and product polysilanes were limited.

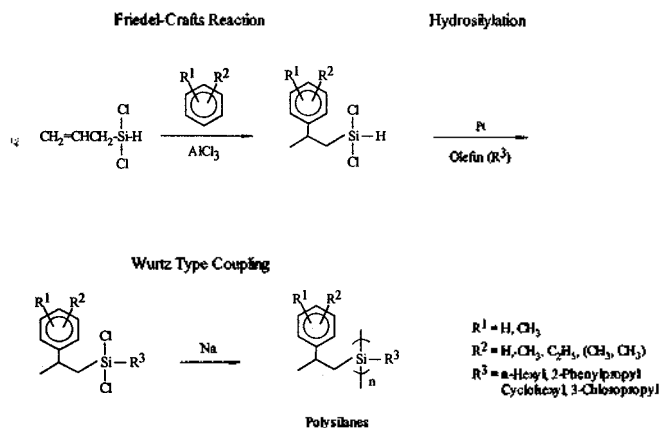
This study describes the syntheses and characterizations of polysilanes with various organic substituents using relatively convenient methods. The organic substituents are rather bulky in size, and expected to cause property changes of polysilanes. The effects of substituents and reaction time are measured and the thermal, electronic, and photochemical properties are discussed.

Experimental

Materials and Physical Measurements. Solvents were dried by distillation over a Na-benzophenone system. Sodium metal was used as received from Aldrich Chemical Co. (U. S. A.) and Cica Chemical Co. (Japan). Other chemicals were used as received from Aldrich Chemical Co.

Allyldichlorosilane, prepared from the direct reaction of allylchloride and metallic silicon with Cu catalyst, was generously donated by Dr. I. N. Jung in KIST.⁹ Dichlorosilanes with two organic substituents, were prepared in series by the Friedel-Crafts reaction and the hydrosilylation reaction, as shown in Scheme 1, and the procedures were described elsewhere.¹⁰

NMR spectra were recorded at room temperature using $CDCl_3$ on a Bruker 200 MHz AM-200-SY and a Varian 300



Scheme 1. Synthesis of Polysilanes.

MHz Gemini 300 instruments. Electronic spectra were measured with a Shimadzu UV3101PC UV-visible-NIR spectrophotometer. Molecular weights were measured with a Waters GPC 590 equipped with three Styragel columns of pore size 500, 10³, 10⁴ Å in series, and a differential refractometer. The molecular weights and polydispersities are obtained using polystyrene standards. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGS-2 under N₂ atmosphere. Heating rate was 10 °C/min over the temperature range of 50-900 °C. Gas-liquid chromatography (GLC) which was employed to identify the reactants and check the purity was a Hewlett-Packard 5890 series II equipped with a thermal conductivity detector and a packed column (OV101, 6 ft). IR spectra were measured with a Bio-Rad Digilab Division model FTS-7 FT-IR instrument.

Synthesis. A 25 mL three-necked, round bottom flask was fitted with a reflux condenser, a pressure equalizing addition funnel and a magnetic stirring bar. All system was thoroughly flame-dried under nitrogen. Toluene (5 mL) and sodium (0.13 g, 5.70 mmol) were added to the flask. After sodium was dispersed into fine particles by heating to a toluene-refluxing temperature with vigorous agitation, (*n*-hexyl)(2-(methylphenyl)propyl)dichlorosilane (0.90 g, 2.84 mmol) was added by the syringe pump for 5 minutes and then the reflux was maintained for 4 hours. When the reaction was completed, liquid portion was separated from solid residues of unreacted sodium and sodium chloride by cannular filtration. After solvent was evaporated, a pale yellow, oily product was treated with *n*-hexane to separate the soluble and insoluble fractions. Insoluble solid was filtered to give 0.19 g (27%) of the solid poly[2-(methylphenyl)propyl](*n*-hexyl)silane [R¹=H, R²=CH₃, R³=*n*-hexyl], and solvent was completely removed from the filtrate to give 0.51 g (72%) of liquid poly[2-(methylphenyl)propyl](*n*-hexyl)silane. Products were characterized by the spectral measurements.

Following polysilanes were similarly prepared. poly(2-phenylpropyl)(*n*-hexyl)silane [R¹=R²=H, R³=*n*-hexyl], poly[2-

(ethylphenyl)propyl](*n*-hexyl)silane [R¹=H, R²=C₂H₅, R³=*n*-hexyl], poly[2-(chlorophenyl)propyl](*n*-hexyl)silane [R¹=H, R²=Cl, R³=*n*-hexyl], poly[2-(dimethylphenyl)propyl](*n*-hexyl)silane [R¹=CH₃, R²=CH₃, R³=*n*-hexyl], poly(2-phenylpropyl)(2-phenylethyl)silane [R¹=R²=H, R³=2-phenylethyl], poly[2-(methylphenyl)propyl](2-phenylethyl)silane [R¹=H, R²=CH₃, R³=2-phenylethyl], poly[2-(ethylphenyl)propyl](2-phenylethyl)silane [R¹=H, R²=C₂H₅, R³=2-phenylethyl], poly[2-(dimethylphenyl)propyl](2-phenylethyl)silane, [R¹=CH₃, R²=CH₃, R³=2-phenylethyl], poly(2-phenylpropyl)(3-chloropropyl)silane [R¹=R²=H, R³=3-chloropropyl], poly[2-(methylphenyl)propyl](3-chloropropyl)silane [R¹=H, R²=CH₃, R³=3-chloropropyl], poly[2-(chlorophenyl)propyl](3-chloropropyl)silane [R¹=H, R²=Cl, R³=3-chloropropyl], poly[2-(methylphenyl)propyl](cyclohexyl)silane [R¹=H, R²=CH₃, R³=cyclohexyl].

UV Photolysis. Polydiorganosilanes were dissolved in freshly distilled tetrahydrofuran and irradiated with UV light. Lamp housing consisted of a medium pressure mercury lamp, a glass filter if necessary, a slit (1 mm×10 mm) and a shutter. Photochemical changes were measured by UV-visible spectroscopy and molecular weight changes were measured by GPC after photolysis.

Results and Discussion

Several linear polysilanes were prepared by Wurtz-type coupling reaction of diorganodichlorosilanes using sodium metal in toluene-refluxing temperature. The polymerization results are shown in Table 1. Generation of polysilane was confirmed by the electronic spectra of the product solutions which gave the characteristic absorption at UV region. Usually the absorption was observed as dual peaks, one λ_{max} in near 280 nm and another λ_{max} near 327 nm as shown in Figure 2. Those UV absorptions are interpreted as σ electron transition through Si-Si backbone. GPC chromatograms of product solution gave bimodal patterns as shown in Figure

Table 1. Syntheses and Characterizations of Polysilanes

No.	R ¹	Substituent		Reaction Time (hr)	Yield (%)		Low MW Polymer		High MW Polymer	
		R ²	R ³		Low	High	λ _{max} (ε _{max} ×10 ⁻³)	M _w (M _n)×10 ⁻³	λ _{max} (ε _{max} ×10 ⁻⁴)	M _w (M _n)×10 ⁻⁶
1	H	H	<i>n</i> -Hexyl	4	66	26	282 (7.63)	1.20 (1.01)	327 (2.33)	2.02 (0.62)
2	H	H	<i>n</i> -Hexyl	7	75	7	282 (7.75)	1.05 (0.93)	327 (2.41)	3.79 (2.44)
3	H	H	<i>n</i> -Hexyl	16	85	4	281 (7.88)	1.16 (0.95)	327 (2.49)	0.93 (0.14)
4	H	Me	<i>n</i> -Hexyl	4	72	27	282 (7.98)	1.25 (1.11)	327 (1.76)	3.47 (1.85)
5	H	Et	<i>n</i> -Hexyl	4	96		282 (7.84)	3.01 (1.79)		
6	Me	Me	<i>n</i> -Hexyl	4	96		282 (5.61)	1.48 (1.25)		
7	H	H	2-Phenylethyl	4	81	13	282 (6.62)	0.84 (0.64)	327 (1.61)	a
8	H	Me	2-Phenylethyl	4	83	8	282 (7.23)	1.06 (0.86)	327 (1.77)	1.73 (0.38)
9	H	Et	2-Phenylethyl	4	88	4	282 (5.54)	1.13 (0.84)	327 (1.69)	3.08 (1.08)
10	Me	Me	2-Phenylethyl	4	87	7	282 (6.03)	1.31 (1.03)	327 (2.19)	2.24 (0.64)
11	H	Me	Cyclohexyl	4	96		282 (5.99)	0.93 (0.72)		
12	H	H	3-Chloropropyl	4	86		282 (4.43)	1.01 (0.79)	322sh, b	
13	H	Me	3-Chloropropyl	4	81		282 (7.51)	1.24 (0.69)		
14	H	Cl	3-Chloropropyl	4	26	60	282 (8.95)	2.85 (1.08)	320sh, b	
15	H	Cl	<i>n</i> -Hexyl	4	44	38	282 (8.19)	2.84 (1.00)	320sh, b	

^aNot measured. ^bShoulder peak was observed with low MW polymer absorption.

1, indicating that the product solutions were mixtures of high- and low-molecular-weight fractions. The mixtures were separated into the low-molecular-weight liquid polymer and the high-molecular-weight solid polymer. Solid high-molecular-weight polymers are soluble in most organic solvents such as toluene except *n*-hexane. But some crosslinked high-molecular-weight polymers (*vide infra*) were insoluble. After separation, UV absorptions and GPC chromatograms were measured again and it was confirmed that the low-molecular-weight polymer showed deep UV λ_{max} at 280 nm and high-molecular-weight polymer showed blue shifted λ_{max} at 327 nm. Therefore it was confirmed that the synthesis of polysilanes with Wurtz-type coupling gave a low-molecular-weight polymer with $\bar{M}_w \sim 10^3$ and λ_{max} at 280 nm, and a high-molecular-weight polymer with $\bar{M}_w \sim 10^6$ and λ_{max} at 327 nm. Comparisons of ^1H NMR and IR spectra of the reactants and polysilane products showed that there was no structural changes except of dechlorination.

The overall yields for polysilanes are 81-99% and \bar{M}_w of the low-molecular-weight polymers are in the range of 900-3,000, \bar{M}_w of the high-molecular-weight polymer are in the

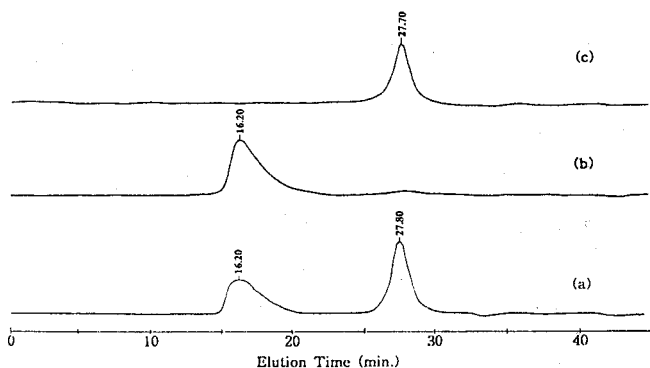


Figure 1. GPC Chromatograms of Poly(2-(dimethylphenyl)propyl)(2-phenylethyl)silane, (a) Reaction Product Solution, (b) High Molecular Weight Polymer, (c) Low Molecular Weight Polymer.

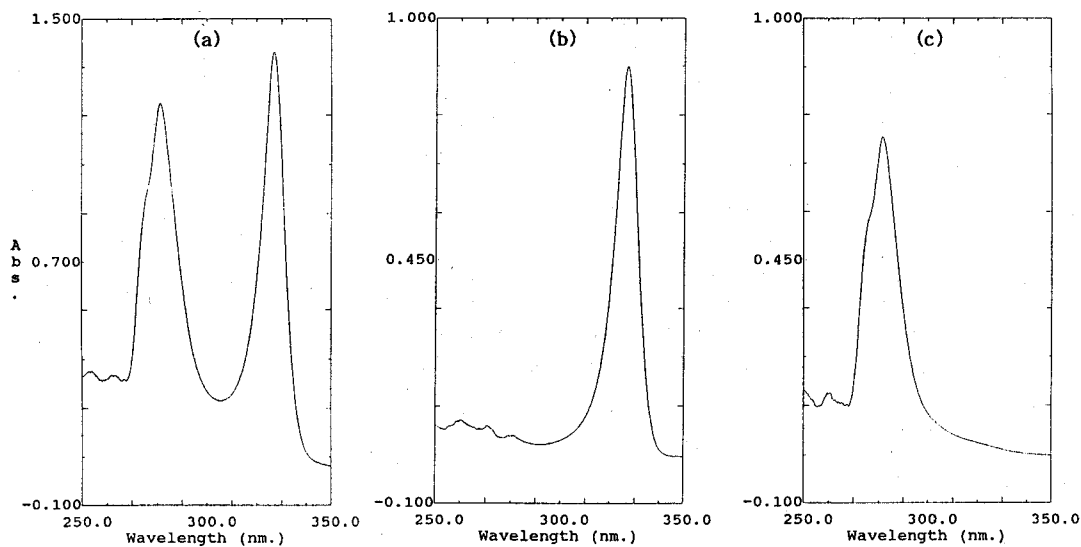


Figure 2. UV Absorption Spectra of Poly(2-(ethylphenyl)propyl)(2-phenylethyl)silane, (a) Reaction Product Solution, (b) High Molecular Weight Polymer, (c) Low Molecular Weight Polymer.

range of 900,000-3,800,000. About 10% loss was assumed as a low-molecular volatile fraction which could be disappeared during the vacuum evaporation of solvent. Poly(2-arylpropyl) silanes, whose substituents are similar to one of substituents in this study, were prepared by the dehydrogenative polymerization and reported the polymers as \bar{M}_w of 700-1,300 range with the yields of 31-84%.¹¹ When this and the present results of the low polymers were compared, it is found that Wurtz-type coupling is more efficient despite of larger steric effect of substituents in poly(2-arylpropyl)(alkyl or aryl-alkyl) silanes. In addition, high polymers were formed up to 27% (soluble polysilanes) or 60% (insoluble polysilanes).

A major product was a liquid low MW polymer and a minor product was a solid high MW polymer. After 4 hours of reflux, reactant was disappeared from reaction mixtures, checked by GLC, indicating completion of reaction. However long reaction time gave an adverse effect to the formation of high MW polymer. (Table 1, # 1, 2, 3) The longer the reflux was, the larger amount of low MW polymer formed and the smaller the amount of high MW polymer formed. In the Wurtz-type condensation reaction, it was assumed that after the certain amount of polymerization was progressed, the chain length was decreased by the back-biting process caused by unreacted sodium.^{13a}

Though it is not prominent, the effect of substituents are observed. (Table 1, # 1, 4, 5, 6) The changes of substituents on the phenyl ring, R^1 and R^2 , from H, Me, Et, (Me, Me) at the same reaction conditions did not change the overall yields. But the formation of high MW polymer was decreased while substituent size was increased. Practically the desired solid product was not observed for the substituents Et and (Me, Me) and it was thought that the small increase of steric hindrance in the already-crowded silanes might give a bad effect to the formation of high MW polymers. Steric effect was also observed when the substituent directly bound to silicon atom (R^3) was changed. Increase of crowdness near silicon atom, *n*-hexyl, 2-phenylethyl, cyclohexyl, decreased the formation of high MW polymers. (Table 1, # 7, 8, 9,

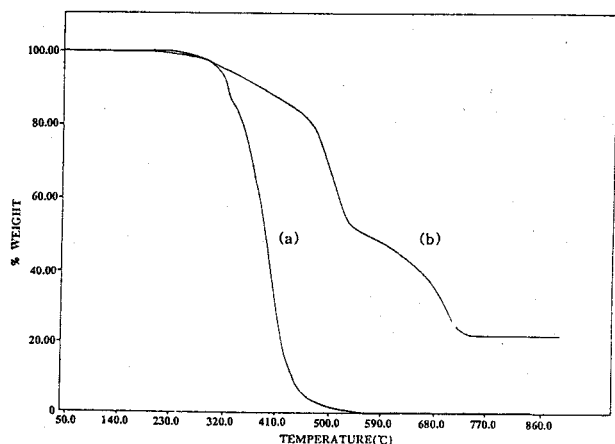


Figure 3. TGA Thermograms of (a) Linear Poly(2-phenylpropyl)(*n*-hexyl)silane, (b) Crosslinked poly(2-(chlorophenyl)propyl)(*n*-hexyl)silane, Under N_2 .

10, 11).

It is interesting to know whether functionalization of polysilane is possible. It may change the properties of polysilanes after polymer formed. (Table 1, # 12, 13, 14, 15) In order to find the possibilities of functionalization, Cl was introduced to the phenyl ring (e.g. R^2) and the substituent directly bound to silicon atom (R^3). However all of Cl in phenyl ring (R^2) could not survive during Wurtz-type dechlorination reaction. It was found that the reaction product was a mixture of high and low MW polymers and that the high MW polymer was not soluble in any organic solvents. Probably some Cl on phenyl ring took part in the Wurtz-type reaction to give the crosslinked, network structure and polysilanes might become insoluble. However NMR spectra of low MW polymer showed that Cl in phenyl ring was intact. Also chloropropyl group in R^3 was remain intact during the synthesis. Though further modification of polysilanes using those Cl was not made in this study, they can be utilized for further functionalization.

For thermal properties of polysilanes, TGA thermograms of soluble poly(*n*-hexyl)[2-(phenyl)propyl]silane and insoluble poly[2-(chlorophenyl)propyl](*n*-hexyl)silane were measured under an inert atmosphere. (Figure 3) Linear polysilane started to degrade at about 300 °C and continued to about 560 °C and no residue was left after 600 °C. All of composition of polysilane even with large and bulky organic substituents on each silicon atom is believed to be converted to volatile components such as organic radicals or monosilanes. This pattern of continuous degradation and complete decomposition is typical thermal property of linear polysilane.¹² On the contrary, the degradation pattern of crosslinked polysilane was different. Thermal degradation took place in two steps and the 21.3% of residue was left after 900 °C. The residue is believed to be silicon carbide and it was resulted from silicon-carbon bond in polysilane which was formed from Wurtz reaction of Si-Cl and phenyl-Cl groups. It was already established that the crosslinked polysilane-polycarbosilane polymers gave the silicon carbide when pyrolyzed.¹³ High ceramic yield of crosslinked polysilane give a good prospect as a ceramic precursor.

As already mentioned earlier, polysilanes give a character-

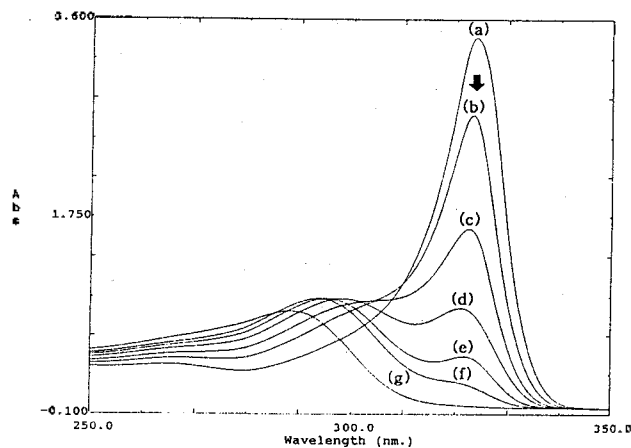


Figure 4. UV Irradiation of Poly(2-(methylphenyl)propyl)(2-phenylethyl)silane Irradiation Time: (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 30, (g) 80 min.

istic electronic transition and it was confirmed that the increase of molecular weight of polysilanes give a bathochromic shift. One of the purpose of changing substituents on polysilanes, R^1 , R^2 , R^3 , in this study was to find the effect of those changes to the electronic transition. However λ_{max} were not changed at all for those various polysilanes, suggesting that electronic effect of substituents was not operating. One interesting thing is that chloropropyl group in R^3 is sterically less hindered than *n*-hexyl group but did not give high polymers against expectation and it may provide electronic effect at the close range. It is known that polysilanes were light sensitive. But it was found that the poly(2-arylpropyl)(alkyl or aryl-alkyl)silanes were degrading even under room light. In order to find the photochemical property of polysilanes, those soluble high MW polysilanes were dissolved in freshly distilled and degassed tetrahydrofuran and irradiated by UV light. The spectral changes were recorded by UV-visible spectrometer. (e.g. Figure 4) Initial absorption at 327 nm decreased by UV irradiation and new λ_{max} at about 300 nm formed. But as irradiation continued, new λ_{max} at about 300 nm moved to shorter wavelength, thereby resulting λ_{max} at about 287 nm. Therefore it was estimated that there were two steps in photochemical reactions with one rather unstable intermediate. Precise mechanism for photochemical reaction was not taken in this study, but photodegradation of a number of substituted polysilanes at 254 nm in solution has been measured and formation of silylenes and silyl radicals were reported.^{11,14} Also spectral bleaching of absorption band at UV region by photodegradation suggested Si-Si bond homolysis.¹⁵ Therefore it could be concluded from the blue shift of λ_{max} and GPC measurement of photochemical product showed that the degradation of polysilane was progressing under UV irradiation. One interesting point is that the photochemical reaction product with λ_{max} at 287 nm in this study was same as the low MW polymer of Wurtz-type reaction.

Conclusion

This work describes the preparations and characterizations of new polysilanes with various substituents by utilizing Wurtz-type coupling reaction. Despite of the bulkiness of the

substituents in polysilanes, linear high MW polymers with \bar{M}_w of $\sim 10^6$ were obtained with yield up to 27%. However the yields of linear high MW polymers were influenced by the steric bulkiness. Those polysilanes shows the characteristic electronic transitions and may used to various applications. Also TGA results of crosslinked polysilanes showed the possibility for a ceramic precursor. Preparation of polysilanes by sonochemical methods and measurements of other properties such as photochemical reactivity, nonlinear optical property are in progress.

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Synthesis and Molecular Structure of Calix[4]arene Butanoate 1,2-Alternate Conformer

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Three conformational isomers of calix[4]arene butanoate were isolated from the reaction of calix[4]arene and butanoyl chloride in the presence of NaH and their structures were determined by NMR spectra as 1,2-alternate **2a**, partial cone **2b** and 1,3-alternate conformer **2c**, respectively. The crystal structure of **2a** has been determined by X-ray diffraction method. The crystals are monoclinic, space group C2/c, $a = 18.435$ (4), $b = 13.774$ (2), $c = 16.941$ (3) Å, $\beta = 116.23$ (1)°, $Z = 4$, $V = 3858.8$ (12) Å³, $D_c = 1.21$ g cm⁻³, $D_m = 1.21$ g cm⁻³. The molecule is in the 1,2-alternate conformation. It has two-fold symmetry axis along the line connecting between C (7AA') and C (7BB') parallel to the b axis of crystal lattice.

Introduction

Calixarenes, a class of synthetic macrocycles having phe-

nolic residues in a cyclic array linked by methylene groups at the position "ortho" to the hydroxy groups, have cavities of sufficient size to form host-guest complexes and thus are