NOTES

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Intramolecular Photocycloaddition of Noncyclic Polyether Compounds Containing α,ω-Dicinnamates End Groups and Uptake of Alkali Metal Thiocyanates with Them[1]

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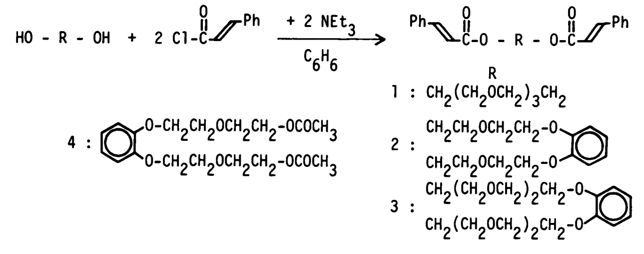
Synopsis. Noncyclic polyethers containing two cinnamoyl end groups have been prepared, they were cyclized by photosensitized intramolecular addition. The uptake of alkali metal (sodium and potassium) thiocyanates with these compounds and their ability to extract has been investigated before and after the cyclization.

Intramolecular photocycloaddition in α,ω-dicinnamates to construct macrocycles has been studied by several groups,[2] but there are few applications of them to prepare cyclic polyethers which exhibit, for example, the extracting ability for cations.[3] Conversion of the noncyclic polyethers to the cyclic ones will bring about a change of the ability in the cation-uptake. In this paper we wish to report the photo-induced intramolecular cyclization of noncyclic oligoethylene glycol derivatives containing cinnamoyl group at both ends of the molecule and the ability of uptake for alkali thiocyanate with them.

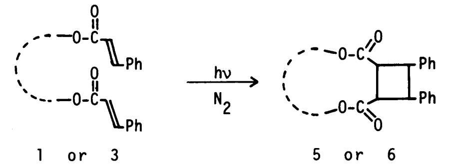
Results and Discussion

As shown in Scheme 1, three noncyclic polyether compounds having two cinnamoyl end groups were prepared by the reaction of an oligoethylene glycol with two mole equivalents of cinnamoyl chloride in the presence of triethylamine. By this procedure, tetraethylene glycol dicinnamate (**1**), 1,2-bis[2-[2-(cinnamoyl)ethoxy]ethoxy]benzene (**2**), and 1,2-bis[2-[2-[2-(cinnamoyl)ethoxy]ethoxy]ethoxy]benzene (**3**) were obtained. 1,2-Bis[2-(2-acetoxyethoxy)ethoxy]benzene (**4**) was also prepared to allow comparison of the abilities of uptake. In Table 1, the analytical data are summarized.



Scheme 1. Preparation of polyethers with two cinnamoyl end groups.

Intramolecular photocycloaddition of biscinnamates (**1**)—(**3**) was carried out by high dilution technique in acetone using a 400-W high pressure mercury lump under bubbling of gaseous nitrogen in the presence of a catalytic amount of benzophenone as a sensitizer (Scheme 2): **5**; yield 27%, NMR ($CDCl_3$) δ=3.4—4.7 (12H, m, cyclobutane ring+oligo(oxyethylene)), 3.67 (8H, s, oligo(oxyethylene)), 7.33 (10H, s, C_6H_5) ppm; and **6**; yield 21%, NMR ($CDCl_3$) δ=3.0—4.5 (24H, m, cyclobutane ring+oligo(oxyethylene)), 6.89 (4H, s, *o*-phenylene), and 7.32 (10H, s, C_6H_5) ppm. But an attempt to prepare the corresponding cycloadduct from **2** was unsuccessful. In the IR spectra, the absorption band based on cinnamoyl C=C double bond (at 1635 cm^{-1} for **1** and **3**) disappeared completely after the photoirradiation. In the proton NMR, the signal



Scheme 2. Intramolecular photocycloaddition of polyethers with cinnamoyl groups.

Table 1. Analytical data of noncyclic polyethers

Polyether	Yield	Elemental analysis			NMR spectrum(δ ppm from TMS in $CDCl_3$)				
	%		H,%	C,%	-CH=CH-	C_6H_5	$-OCH_2CH_2O-$	o-C_6H_4	CH_3
1	65	Found Calcd	6.40 6.65	68.26 68.71	6.48(d) 7.70(d) (10 Hz)	7.41	3.70(s) 3.77(t) 4.35(t)	—	—
2	73	Found Calcd	6.19 6.27	69.70 70.32	6.47(d) 7.65(d) (10 Hz)	7.42	3.8—4.6 (m)	6.93(s)	—
3	62	Found Calcd	6.60 6.67	67.95 68.12	6.50(d) 7.80(d) (10 Hz)	7.43	3.73(s) 3.6—4.5 (m)	6.92(s)	—
4	58	Found Calcd	7.02 7.08	57.59 58.37	—	—	3.84(m) 4.17(m)	6.93(s)	2.07(s)

Table 2. Solubilization of thiocyanate salts into CH_2Cl_2

Polyether	Amount of solubilized thiocyanates (mol of MSCN/mole of polyether)[a]	
	NaSCN	KSCN
1	0.12	≈0
2	0.22	≈0
3	0.48	0.53
4	0.21	≈0
5	0.21	0.03
6	0.45	0.34

a) The values were calculated from elemental analysis.

of the olefin proton of **1** disappeared in **5** and the signal for the cyclobutane ring protons appeared at around 4 ppm. The stereochemistry at the point of closure could not be elucidated from the cyclobutane protons since these were obscured by other oxyethylene protons. But it is presumed that such macrocyclic ring-closure in solution phase may be δ-addition(anti, head to head) according to the literature.[2b] In addition, the mass spectroscopic data confirmed that the molecular weights of **5** and **6** are exactly the same as those of **1** and **3**, respectively.

Thus, the ability of uptake for sodium and potassium thiocyanates with these compounds was examined. After we mixed the polyether and powdered alkali thiocyanate in dichloromethane at room temperature, we determined the amount of alkali thiocyanates solubilized into the solvent by elemental analysis (see Experimental). The results are shown in Table 2. The 17-membered ring compound (**5**) can uptake NaSCN two times better than **1**, whereas both **1** and **5** can uptake very little KSCN. Noncyclic polyether (**3**), which has a longer oxyethylene moiety compared with **1**, exhibits better uptake for K^+ salt than that for Na^+ salt. On the other hand, the 26-membered ring compound (**6**) can solubilize Na^+ salt a little more than K^+ salt.

Contrary to our expectation, the difference in the selectivity and ability of uptake between cyclic and noncyclic compounds was not so large. It could be considered that the cyclobutane structure bearing two ester groups largely distorts the cyclic polyether structure and therefore their ability of uptake can not be improved distinctly compared with that of noncyclic ones. Furthermore, it has been reported that the metal ion complexing properties of crown ethers containing ester groups are generally different from the corresponding ones which are formed from ethylene glycol units.[4] Our failure may be attributed to the introduction of both cyclobutane ring and two ester groups into a macrocyclic system.

In the extraction of alkali salts by noncyclic polyethers, (**1**)—(**4**), the longer the oxyethylene chain is, the better the ability of uptake is. It means that in this case the structure of end groups of these noncyclic polyethers has little effect on their ability of uptake.

Experimental

The 2-(2-chloroethoxy)ethanol and 2-[2-(2-chloroethoxy)-ethoxy]ethanol were commercially available (Aldrich Chem. Co.) and were used without further purification. The NMR and IR spectra were recorded on a Varian EM-360 (60 MHz) using TMS as the internal standard and on a JASCO IRA-1 infrared spectrometers, respectively. The mass spectrum was measured with a Hitachi M-52 mass spectrometer.

General Procedure for the Preparation of Noncyclic Polyethers. 1,2-Bis[2-(2-hydroxyethoxy)ethoxy]benzene and 1,2-bis[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene were prepared by the reaction of catechol with 2 mole equivalents of 2-(2-chloroethoxy)ethanol and 2-[2-(2-chloroethoxy)ethoxy]ethanol, respectively, in the presence of powdered potassium carbonate in DMF. Then, to the benzene of the mixture of 1 mole equivalent of the oligoethylene glycol and 2 mole equivalents of triethylamine was added dropwise 2 mole equivalents of cinnamoyl chloride at room temperature. After the solution was stirred for 12 h at room temperature, the solution was washed with water and dried with magnesium sulfate. After removal of benzene by evaporation, the residue was submitted to column chromatography(chloroform) on silica gel.

General Procedure of Irradiation. Irradiations on a preparative scale were performed with Pyrex-filtered light from a 400-W high pressure mercury lamp (Riko) under bubbling of gaseous nitrogen in an immersion apparatus.

Preparation of 5. An acetone (250 ml) solution of 1.3 g of **1** and 0.01 g of benzophenone was irradiated in the Pyrex cell described above at 40 °C for 7 h. After solvent was removed, the remaining reaction products were isolated by column chromatography on alumina. The first elution with chloroform gave a colorless oily product, **5**, which was identified with IR, NMR, and mass spectroscopic method and elementary analysis. The other product were also oily and seemed to be intermolecular adducts(oligomeric products) because of their high viscosity. Further identification was not done.

In a similar manner, a cyclic product, **6**, was isolated.

Extraction Procedure. In a typical experiment, to the solution (0.1 g of the polyether prepared in 5 ml of dichloromethane) 0.5 g of alkali thiocyanate powder was added, and then the mixture was stirred for 12 h at room temperature. The insoluble salt was filtered off and the solvent was evaporated from the filtrate. The amounts of alkali thiocyanate solubilized into dichloromethane was determined by elementary analysis. The results are summarized in Table 2. Under these conditions, thiocyanate salts in the absence of the polyether did not dissolve in dichloromethane at all.

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