

41-9; **2d β** , 123-11-5; **4a**, 78018-66-3; **4b α** , 117096-03-4; **4b β** , 117096-02-3; **4c α** , 117096-05-6; **4c β** , 117096-04-5; **4d α** , 117096-07-8; **4d β** , 117096-06-7; **4e β** , 117096-08-9; **4f**, 117096-09-0; **4g**, 117096-10-3; **4h β** , 117096-11-4; **4i α** , 14435-89-3; **7** ($R^1 = \text{Ph}$, $R^2 = \text{Me}$), 29076-84-4; **7** ($R^1 = p\text{-tolyl}$, $R^2 = \text{Me}$), 94115-03-4; **8**, 3693-53-6; **9**, 116916-17-7; 2-methyl-1-phenyl-3-*p*-tolylprop-2-en-1-one, 78451-39-5; 1,3-diphenyl-2-methylprop-2-en-1-one, 4258-37-1.

Supplementary Material Available: Spectral data for **4c β** , **4c α** , **4d β** , **4d α** , **4e β** , **4f**, and **4g** (2 pages). Ordering information is given on any current masthead page.

A One-Step Route to (*E*)-1,2-Bis(9-anthryl)ethene

Melanie J. Cravey* and Denaha J. Doss

Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77553

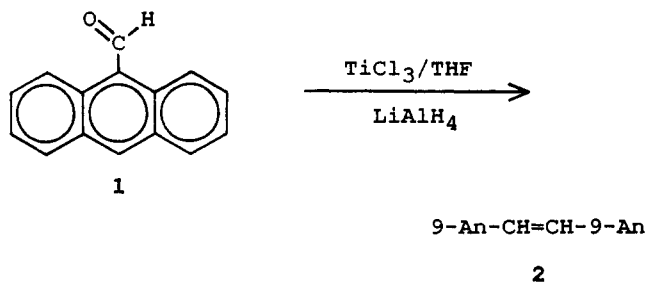
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Recently there have been several groups interested in the structure and properties of sterically crowded alkenes.^{1,2} Among these are the 1,2-bis(9-anthryl)ethenes, which are apparently not planar due to the steric interactions between the vinyl and the anthryl 1 and 1' hydrogens.² The McMurry titanium coupling reaction³ has shown remarkable utility for the synthesis of such compounds, having been used successfully for many of the compounds of interest.¹ However, in spite of the several routes noted in the literature for the preparation of 1,2-bis(9-anthryl)ethene,⁴ the titanium coupling reaction has not been among them. We report here a simple one-step route to this compound from commercially available 9-anthraldehyde, thereby avoiding any prior preparation of difficult starting materials.

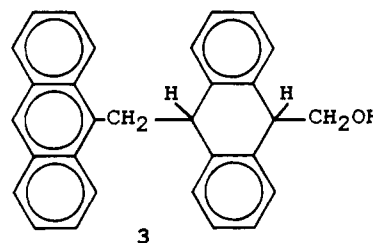
The low valent titanium coupling reaction has been described by McMurry³ and others. The reaction is known to work well for a variety of ketones and aldehydes, even for the preparations of some of these crowded alkenes.¹ However, Geise⁵ and Olah,^{1d} for example, have noted some failure of the reaction for ketones where the carbonyl is excessively crowded sterically in its approach to the titanium surface. In these examples coupling either failed completely^{1d,5} or led to a coupled symmetrical alkane,⁵ where deoxygenation of the intermediate pinacol had occurred, but not to form the desired alkene. Lenoir^{1a} made the only mention of a similar problem for an aldehyde, finding steric crowding for trimethylacetaldehyde. In this example the intermediate pinacol formed but was never deoxygenated to form the desired alkene or an alkane.

The primary goal of our research is the synthesis of electroactive polymers. We wished to apply the titanium coupling reaction to aromatic carbonyl compounds for the preparation of extended π -network systems. The 9-anthraldehyde (**1**) was chosen as a model compound. We

felt that the steric requirements for 9-anthraldehyde would make it feasible to try this reaction as a quick route to the desired 1,2-bis(9-anthryl)ethene (**2**).



Interestingly, one other possible side reaction must be considered. It has been reported in the literature^{6,7} that 9-anthraldehyde reacts with lithium aluminum hydride in THF to form an alcohol, but not the expected 9-(hydroxymethyl)anthracene (which is observed when the reaction is run in diethyl ether).⁶ Instead a type of dimer forms, found to be 9-(hydroxymethyl)-10-(9-anthrylmethyl)-9,10-dihydroanthracene (**3**), later proven by X-ray diffraction.⁸ The earlier literature reports of 1,2-bis(9-anthryl)ethanol⁶ were apparently in error.⁷ In any event, our use of LiAlH_4 in THF for the coupling reaction meant a careful search for this other type of dimer must be made.



The experiment was run in the manner described by Geise.⁵ One equivalent of LiAlH_4 (0.006 mol, 0.23 g) was added in small portions to 2 equiv of TiCl_3 (0.011 mol, 1.70 g) prechilled to 0 °C in 100 mL of THF (distilled from LiAlH_4 and stored over Na). This mixture was stirred for 30 min cold and then was raised to reflux for another 30 min. The 9-anthraldehyde (2 equiv, 0.006 mol, 1.24 g, Aldrich) dissolved in 50 mL of THF was added dropwise, and refluxing was continued for 20 h (a) or for 211 h (b).⁹ After the reaction mixture was quenched with 40 mL of 2 N HCl, the product began precipitating and was collected by vacuum filtration.

The yields of 1,2-bis(9-anthryl)ethene from reactions a and b were modest, 28% and 53%, respectively. In view of the known twist of the anthracenes out of the plane of the ethylene² this is a fairly sterically crowded olefin. It was therefore noteworthy to achieve even these modest yields, if one considers the failure of this reaction to form the olefin from trimethylacetaldehyde, as reported by Lenoir^{1a} to stop at the diol. The other sterically crowded olefin syntheses typically have low yields, cf. the yield observed by Olah⁷ for the tetraeneopentylethylene of 38%. Without further purification our 1,2-bis(9-anthryl)ethene had a melting point of 335–340 °C (lit. mp 350,^{4c} 338,^{4a} and

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(9) Authors' note: results from a similar molecule indicated that no significant improvements in yield could be seen prior to at least 5 days of reaction time.

335 °C^{4b}) and an elemental analysis: C, 94.59; H, 5.39 (calcd: C, 94.70; H, 5.30).

Not surprisingly, the trans isomer is the only product observed. One indication is the melting point. This cis isomerizes to trans at 215 °C,^{4c} and we saw no evidence for this in our product. The 270-MHZ ¹H NMR data matched that reported by Becker^{4c} and Mislow¹⁰ for the trans isomer. We also noted the appearance of an IR peak at 980 cm⁻¹, characteristic of trans alkenes.

We have ascertained that the remainder of the starting material was unchanged (by TLC and IR data). Although increasing the reaction time almost doubled the yield, the length of time is too long to consider trying for further improvement. We have also made a careful search (using IR and NMR) for any of the dimeric alcohol product reported in the literature,^{6,7} with negative results.

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Registry No. 1, 642-31-9; 2, 3849-11-4.

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Synthesis and Complexing Ability of N-Alkylmorpholino Crown Ethers and Their Derivatives

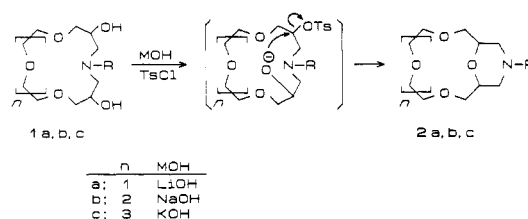
Isao Ikeda, Keiji Kohmoto, Yoshihide Ozawa,
Hideo Kurosawa, and Mitsuo Okahara*

Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka, Japan 565

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Crown ethers that bear a reactive group such as hydroxyl,¹⁻¹¹ amino,^{12,13} or haloalkyl¹⁴ are important compounds for the formation of polymer-bound crown ethers, bis-crown ethers, lariat ethers, and other functionalized crown ethers. Easily prepared dihydroxy monoaza crown ethers 1¹⁵ are also useful functionalized crown compounds,

Scheme I



which can be transformed into cryptands¹⁶ or polymers. In addition, their higher alkyl chain derivatives show interesting surface active behavior in aqueous solution.¹⁷

We report the synthesis and cation binding properties of novel morpholine ring-fused crown ethers 2, which can be easily prepared from 1 in good yield. These morpholino crown ethers 2 are anticipated to have selective and high complexing abilities toward alkali metal cations due to their highly symmetrical structures and rigid conformations. In contrast to aza crown ethers, chemical modifications on the nitrogen atom may be expected to produce only minor interference of the metal cation-binding property of the crown ring since the nitrogen atom is not located in the crown ring. Such modifications may give hydrophilic character to the lipophilic alkyl-substituted crown ethers and make them applicable as amphiphilic compounds or ionophores with controlled water solubility.

Results and Discussion

Dihydroxy monoaza crown ethers 1 were prepared by the reaction of equimolar amounts of oligoethylene glycol bis(glycidyl ether)¹⁸ and primary amines in methanol, according to the method reported previously.¹⁵

N-Alkylmorpholino crown ethers 2 were prepared as pale yellow liquids by adding a dioxane solution of equimolar 1 and tosyl chloride to a suspension of excess pulverized alkali metal hydroxide in dioxane.

Lithium, sodium, and potassium hydroxides were found to produce the best cyclization yields of 12-crown, 15-crown, and 18-crown ethers, respectively, showing an apparent template effect of the alkali cations. A reaction pathway similar to that suggested for the cyclization of oligoethylene glycols to crown ethers^{19,20} is proposed (Scheme I).

Product 2 should be composed of stereoisomers, which may have potentially different binding properties. This situation is reminiscent of the isomer problem of dicyclohexano-18-crown-6.²¹ Distortionless enhancement by polarization transfer (DEPT) ¹³C NMR spectra showed the presence of two kinds of methine carbons at 74.4 and 69.6 ppm for 2b and 69.4 and 65.4 ppm for 2b-HCl, respectively (77.0 ppm for CDCl₃). These two signals should represent the presence of cis and trans isomers, respectively. From single-pulse hetero decoupling without NOE (NNE), the ratios of these signal areas were 1.00:1.21 for 2b and 1.00:0.91 for 2b-HCl. In general, the signal at a lower field is generated in the trans isomer. But in this case, it cannot be concluded which signal corresponds to which isomer, since the area ratios are reversed for 2b and 2b-HCl. ¹H NMR spectra of 2b also show the presence of two isomers.

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